# HETEROGENEOUS EQUILIBRIA BETWEEN AQUEOUS AND METALLIC SOLUTIONS

## THE INTERACTION OF MIXED SALT SOLUTIONS AND LIQUID AMALGAMS

## A STUDY OF THE IONIZATION RELATIONS OF SODIUM AND POTASSIUM CHLORIDES, BROMIDES AND IODIDES IN MIXTURES

BY

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Lansing S. Wells.

# I INTRODUCTION

1. Purpose of the Investigation. This investigation was undertaken with the object of studying the equilibrium between mixed sodium and potassium salts and liquid amalgams as represented by the reversible reaction

$$KHg_m + NaX \rightleftharpoons KX + NaHg_n + (m-n)\ Hg$$

where the free mercury is present in such quantity that its concentration may be taken as constant, and where NaX and KX represent the halides: the chloride, bromide or the iodide. This investigation is the sixth of a series being carried out in this laboratory (1) by a method which was originally developed by G.McP. Smith (2).

2. Constitution of the Mercurial Phase. The metals of the alkali and alkali-earth groups, inclusive of ammonium (3), were long regarded as capable of forming definite chemical compounds (hydrargyrides) with mercury (4). But after Ramsay's (5) calculations of the molecular weights of certain metals in mercurial solution from vapor pressure changes, the view-point gained prevalence that metals of the alkali and alkali-earth groups, as well as others, occur in liquid amalgams in the monatomic condition. While there is good evidence for the non-existence of definite compounds of mercury in the case of certain dissolved metals, such as zinc, cadmium, bismuth, lead and tin, there is, however, in the case of the alkali and alkali-earth metals definite evidence that the dilute amalgams are mercurial solutions of intermetallic compounds of the general formula $Me\ Hg_x$ (6).

But since these metals, even in the dilute liquid amalgams, have certain solution tensions or tendencies to enter into aqueous solution in the ionic condition, the intermetallic compounds must be regarded as slightly dissociated in the sense of the equation

$$\mathrm{Me\ Hg}x \rightleftharpoons \mathrm{Me} + x\ \mathrm{Hg}\ (7). \qquad (1)$$

## 3. Some Principles Relating to the Ionization of Salts.

When Arrhenius proposed the ionic theory it was with the idea of explaining the anomalous behaviour of the colligative properties of aqueous solutions which conduct electricity and the behaviour of such solutions at present find their only successful interpretation in this theory, which involves necessarily a knowledge of the different ionic species present, as well as of their concentration.

The failure of the application of the different methods to determine the degrees of ionization, namely the methods involving colligative properties, and the conductivity method of Arrhenius may be attributed to the occurrence of complex chemical processes between the different molecular species in solution, the nature and extent of which are by no means well known.

In addition to their tendency to unite with water many electrolytes in solution possess the property of uniting with other electrolytes or with non-electrolytes to form complex compounds which ionize to give complex ions. For example potassium ferrocyanide, $K_4[Fe\ (CN)_6]$, $3H_2O$, neglecting the water, ionizes thus

$$K_4[Fe(CN)_6] \rightleftharpoons 4\ K^+ + Fe(CN)_6^{----}$$

giving the very stable complex ion, $Fe(CN)_6^{----}$.

There are many examples of salts that crystallize from aqueous solutions with water of crystallization, as for example, $BaCl_2, 2H_2O$. Undoubtedly these hydrated compounds exist, in part at least, as such in the aqueous solutions, and very likely also yield intermediate and complex ions in such solutions in varying quantities or degrees of stability. There is good evidence that many complexes exist in solution that are not sufficiently insoluble or stable to be separated in the free state. Since under special conditions such a simple salt as potassium chloride, KCl, may crystallize from an aqueous solution with water of crystallization, $KCl, 2H_2O$, we may logically assume that in solution it also contains water molecules, and we also have evidence that points to the hydration of ions. The dissociation or ionization of this simple salt may be represented then by the following equation

$$KCl\ (solid) \rightleftharpoons KCl(H_2O)_x \rightleftharpoons K(H_2O)_y^{\ +} + Cl(H_2O)_z^-$$

In the case of mixtures of strong electrolytes the possibility for the formation of complexes is further increased and the general problem of calculating the degree of ionization of the strong electrolytes become a very complicated one. It is often attached by calculating the degree of ionization on the basis of the isohydric principle ofArrhenius in which the assumption is made that the degree of ionization of each electrolyte in the solution is equal to the value which that electrolyte has in its own solution at the concentration equal to the sum of the concentration of the mixed electrolyte in solution. From the conductivity data available for a large number of mixed salts, in the work of Arrhenius(8), Barnwater (9), MacGregor, Archibald, McIntosh and McKay (10), Sherrill (11), and Sadonnini (12) it has

been found that this assumption agrees fairly well with the experimental data.

However, by means of transference experiments carried out with mixed solutions containing potassium chloride and sulfate, McKay (13) has shown that, although the ratio of the actual partial conductances of the two salts is 7.5% larger than the isohydric principle would require, the observed conductance of the mixture differs by only about 1% from the sum of the calculated partial conductances.

More recently, Loomis and Meacham (14) have shown that, within the limits of our knowledge of a contact potential of the system

$$0.1N\ HCl - 0.1N\ KCl$$

that at 0.1N concentration hydrochloric acid and potassium chloride have approximately the same degrees of ionization. However, from the results of electromotive-force measurements Loomis, Essex and Meacham (15) conclude that the isohydric principle does not apply rigidly (even at 0.1N concentration in this case) and that there is a slight increase in the ionization of the hydrochloric acid as its fraction in the mixture decreases.

It has been shown by the interaction of mixed salt solutions that in equivalent mixtures of sodium and strontium chlorides the ion fraction of the strontium decreases, while the ion fraction of the sodium correspondingly increases, with the increasing total salt concentration (16) and in the case of equivalent mixtures of potassium and strontium chlorides the ion fraction of the potassium correspondingly increases, with increasing total salt

concentration (17). In the case of two simpler salts, those of sodium and potassium, Smith and Ball (18) have found that the sodium ion fraction gains upon that of the potassium as the concentration is increased. This same conclusion has been reached in this present investigation as will be shown later. These ion-fraction changes may be due to any of the following causes: the existence of intermediate ions; the existence of hydrated ions, and the existence of complex ions.

It would appear, then, that the usual methods of studying ionization- colligative properties, conductance, transference, and electromotive-force measurements and others - offer no satisfactory evidence concerning the ionic relationships of strong electrolytes, either singly or in mixtures, except in some cases of very dilute solutions.

## II THEORETICAL

When a liquid potassium amalgam is placed in contact with a sodium salt in aqueous solution, the potassium, owing to its solution tension, tends to pass into the solution in the ionic condition, and there results a difference of potential between the amalgam and the aqueous solution. The amalgam becomes negatively charged and attracts the positive ions of the solution, and, in case impurities are not present, sodium ions alone are discharged into the amalgam; this action continues until the solution tension of the sodium in the amalgam has assumed a value sufficiently great to prevent the further entrance of sodium from the aqueous solution. At this point, equilibrium is established. It has been shown that this reaction is reversible, and that the same equilibrium may be approached in the opposite direction (19). Therefore, the reaction may be represented by the equation

$$K_{Hg} + Na_{H_2O} \rightleftharpoons Na_{Hg} + K_{H_2O},$$

or, since only the free atoms and ions of the metals are supposed to take a direct part in the reaction

$$K^{\circ} + Na^{+} \rightleftharpoons Na^{\circ} + K^{+} \qquad (2) .$$

where $K^{\circ}$ and $Na^{\circ}$ represent the free atoms of potassium and sodium, and $Na^{+}$ and $K^{+}$ the simple, free ions.

We may formulate this equilibrium into the following mass-law expression:

$$\frac{(K^\circ)\ (Na^+)}{(Na^\circ)(K^+)} = k \text{ or } C_o{}^* , \qquad (3)$$

in which $(K^\circ)$ and $(Na^\circ)$ represent the mol fractions of free, uncombined potassium and sodium in the mercurial solutions, and $(K^+)$ and $(Na^+)$ the simple ion fractions of these metals in the aqueous solutions.

This mass-law expression may also be derived from a thermodynamic consideration of the equilibrium. The free-energy decrease attending the transfer at the temperature T of N mols of a substance from an infinite quantity of solution in which its vapor-pressure is $p_1$ and its mol fraction is $x_1$, into an infinite quantity of another solution in which its vapor-pressure is $p_2$ and its mol-fraction is $x_2$ is given by the expressions:

$$-\Delta F = NRT \log_e \frac{p_1}{p_2} \ ; \text{ and } -\Delta F = NRT \log_e \frac{x_1}{x_2}$$

The first of these expressions holds true whatever the concentrations of the substances, provided its vapor conforms to the perfect-gas law; the second holds true when, in conformity either with Raoult's or with Henry's law, the vapor-pressures are proportional to the mol fractions.

Employing the conceptions introduced by Lewis (20) in his system of thermodynamic chemistry, let us represent the fugacity,

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*It has been thought advisable to go back to the letter k (or K) as in the original formulae in place of the symbol $C_o$ which has been used in the last three papers on this work to indicate that the solution of the mixed salts is infinitely dilute - a condition we no longer assume.

or the "escaping tendency", of the uncombined sodium atom in the mercurial solution by the symbol $f_{Na}°$ and the fugacity of the sodium ion in aqueous solution by $f_{Na^+}$. If $\Delta F$ is the free-energy change accompanying the transfer of one atom of sodium from the dilute mercurial solution to the ionic state in an aqueous solution, we may write the following evident relation,

$$-\Delta F_1 = RT \log_e \frac{f_{Na°}}{f_{Na^+}}$$

In the similar transfer of an atom of potassium, we have

$$-\Delta F_2 = RT \log_e \frac{f_{K°}}{f_{K^+}}$$

Since at equilibrium the total free energy change is zero, or, $-\Delta F_1 = -\Delta F_2$, then,

$$RT \log_e \frac{f_{Na°}}{f_{Na^+}} = RT \log_e \frac{f_{K°}}{f_{K^+}}$$

or,

$$\frac{f_{K°}\, f_{Na^+}}{f_{Na°}\, f_{K^+}} = 1. \qquad (4)$$

Investigations (21) indicate that ideal solution laws may properly be applied to very dilute amalgams. For all ordinary aqueous solutions, over wide ranges of concentration, the fugacity of the ionic species is approximately proportional to its concentration (22). On the other hand the fugacity of the undissociated electrolyte is far from proportional to its concentration (23).

Assuming, then, that the ratio of the fugacities of two ions in mixtures varies directly as the ratio of the true ionic concentrations, not necessarily those determined by conductivity,

and replacing the values of the fugacities of the metal atoms in the mercurial solution by the mol fractions of the free amalgamated metals, Equation 4 becomes,

$$\frac{(K^\circ)\ (Na^+)}{(Na^\circ)\ (K^+)} = k$$

which is identical with Equation 3.

Since sodium or potassium even in a very dilute amalgam has a certain solution tension, or tendency to enter into aqueous solution in the ionic condition, the solute in either of these amalgams must be regarded as being slightly dissociated, in the sense of Equation 1,

$$NaHg_n \rightleftharpoons Na^\circ + n\ Hg$$

or,

$$KHg_m \rightleftharpoons K^\circ + m\ Hg\ .$$

The mass-law expressions for these reactions are

$$\frac{[Na^\circ]\ [Hg]^n}{[Na\ Hg_n]} = \text{const., and } \frac{[K^\circ]\ [Hg]^m}{[KHg_m]} = \text{const.}$$

Or, in the very dilute amalgams, in which free mercury is present in such quantity that its concentration may be taken as constant, we have

$$\frac{(Na^\circ)}{(Na_{Hgn})} = \text{const., and } \frac{(K^\circ)}{(K_{Hgm})} = \text{const.}$$

Assuming that these expressions hold true in amalgams containing both metals, we obtain

$$\frac{(K^\circ)}{(Na^\circ)} = \frac{(KHgm)}{(NaHgn)} = \frac{(K^\circ)\ +\ (KHgm)}{(Na^\circ)\ +(NaHgn)} = \frac{(K_{Hg})}{(Na_{Hg})} \qquad (5)$$

and, substituting the value $\frac{(K_{Hg})}{(Na_{Hg})}$ for $\frac{(K^\circ)}{(Na^\circ)}$

in equation 3, we obtain the expression

$$\frac{(K_{Hg})(Na^+)}{(Na_{Hg})(K^+)} = k \qquad (6)$$

Now, in any individual mixed salt solution, the ratio of the salt fractions must bear some numerical relationship to the ion-fraction ratio, or

$$\frac{(NaX)}{(KX)} = n\,\frac{(Na^+)}{(K^+)}\,, \qquad (7)$$

in which the value of n is unknown and may, of course, vary with the conditions of salt concentration.* But, whatever the value of n may be at any specific composition of the mixture, it follows from the preceding equations that, in the case of any particular equilibrium mixture,

$$\frac{(K_{Hg})\ (NaX)}{(Na_{Hg})(KX)} = n\ k = C_c \qquad (8)$$

The values of $(K_{Hg})$ and $(Na_{Hg})$ may readily be calculated from the analytical data of the equilibrium amalgams, and (NaX) and (KX) are known concentration fractions of sodium and potassium chloride, bromide, or iodide. Thus it is possible to calculate

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*. Since only the free atoms and the simple unhydrated ions of the metals are supposed to take a direct part in the equilibrium (in the sense of equation 2) and since we do not know whether the degrees of dissociation of the hydrated (and saltated) ions of sodium and potassium into the simple unhydrated ions are identical, we can not determine the value of n.

$C_c$, the "equilibrium expression" at any specific salt concentration.

By definition,

$$(Na^+) + (K^+) = 1$$

Combining this with Equation 6, we obtain

$$\left.\begin{aligned} \frac{(K_{Hg})(Na^+)}{(Na_{Hg})(K^+)} &= k \\ (Na^+) + (K^+) &= 1 \end{aligned}\right\}$$

and solving, we get

$$(K^+) = \frac{(K_{Hg})}{(K_{Hg}) + k(Na_{Hg})}, \quad \text{and} \qquad (9)$$

$$(Na^+) = 1 - (K^+).$$

If, therefore, a means could be found of obtaining the value of k, we shall be able to calculate the ion-fraction values of sodium and potassium in the mixed solutions.

## III. MATERIALS, APPARATUS AND METHOD OF EXPERIMENTATION

### 1. Materials

The decomposition of the amalgams by the water of the salt solutions is catalyzed by dust particles on the surface of the mercury or by heavy metals contaminating the solution or the amalgam. It is imperative in this work to use only the purest of materials.

(a) Water, Mercury, Chloroplatinic Acid, Sodium Chloride and Potassium Chloride. - These materials were purified according to methods already described in a preceding paper of this series (18).

(b) Sodium Bromide, NaBr, $2H_2O$.- The pure commercial salt was recrystallized from hot distilled water. The mother liquor was removed as completely as possible by suction at the water pump, after which the remainder was thrown off in a high speed electrical centrifuge. A second crystallization was made from pure water, and the mother liquor removed as before. After this the crystals were dried for several days over calcium chloride, and the hydrated salt finally placed in tightly stoppered bottles.

(c)Potassium Bromide.- A good grade of commercial salt was recrystallized twice from hot water as described above. The salt was then dried in a platinum dish in an electric oven at 150°. Just before use it was heated in the dish in an electric muffle furnace for at least two hours at a temperature just short of fusion. It was cooled in a desiccator over calcium chloride.

(d)Sodium iodide, $NaI, 2H_2O$.- The pure commercial salt was recrystallized three times from hot water as described in the purification of sodium bromide. After this the crystals were dried for several days over calcium chloride, and the hydrated salt finally placed in tightly stoppered bottles.

(e)Potassium iodide.- A pure grade of commercial salt was recrystallized from two to three times from hot water. The samples were then dried in an electric oven for several hours at 150°, and finally placed in tightly stoppered bottles.

(f) Amalgams.- The amalgams were prepared by the electrolysis of saturated salt solutions, as described by Smith and Bennett (24). Fairly concentrated liquid amalgams were prepared and analyzed. Before use they were diluted with mercury to the specific concentration desired.

## 2. Apparatus

A description of the apparatus used in this investigation may be found in the paper by G. McP. Smith and T.R. Ball, to which reference has already been made; no change was found to be necessary.

## 3. Method of Experimentation

(a) Solutions.- Separate solutions of the NaX and KX (in which X represents chlorine, bromine, or iodine) were made up each equal in concentration to the total concentration of these mixed salt solutionsdesired. By mixing these solutions in the proper volume relations, in bottles of "Resistenz" glass, it was possible

to prepare solutions of any salt-concentration ratio desired and of the given total concentration.

In the case of the sodium chloride, potassium chloride or potassium bromide, the pure dried salt was weighed out in the calculated quantity, dissolved in pure water, and the solution transferred quantitatively to a calibrated volumetric flask, where it was diluted to the mark at 25°.

In the case of the potassium iodide, sodium iodide, or sodium bromide, the salt was weighed out in sufficient quantity to give a solution slightly more concentrated than desired. This amount was dissolved in water, diluted to a convenient volume, and the normality determined by the Volhard volumetric method. The solution was then accurately diluted to the desired normality.

(b) Equilibrium.- In order that, at the start of each run, the amalgams should be as nearly as possible of the same equivalent concentration, the analyzed stock amalgams were diluted with mercury to the specific concentration desired. The mercury for dilution was weighed out into the counterpoised reaction flask, on a small trip balance, with an accuracy of 0.1-0.2 g. Fifty cubic centimeters of the mixed salt solution were added and the whole counterpoised again; finally, the calculated quantity of the stock amalgam was added. The flask containing the reaction mixture was immediately placed in the thermostat, and shaken for fifteen minutes, after which the mixed salt solution was decanted from the amalgam; a fresh portion of the solution was added, the flask again shaken in the thermostat for fifteen minutes, and the solution again decanted. In the runs where very diluted mixed

salt solutions were used, the amalgams were treated as described above with as many as ten successive portions of the solution; in most cases only six renewals were required; while in the case of the more concentrated solutions still fewer renewals were required to bring about the desired equilibrium. The stock solution was of course kept in the thermostat except when a change was being made.

After decanting the last portion of the solution, the amalgam was in each case washed with water, and decomposed with hydrochloric acid, according to the procedure described in an earlier paper (18). Each run was made with six separate reaction mixtures, three of which were started with sodium amalgam and three with potassium amalgam. In all six cases the mixed salt solutions were identical. In each run, therefore, equilibrium was approached three times from each side.

(c) Treatment of the Decomposition Products.- The hydrochloric acid solution containing the sodium and potassium from the equilibrium amalgam was in each case drawn off quantitatively from the mercury and evaporated to dryness in a weighed platinum or porcelain dish on the steam bath. The mixed sodium and potassium chlorides were dried in the electric oven for at least two hours at 160° (18), and weighed. The mercury itself was dried, and weighed to within 0.1-0.2 g.

(d) Separation of Sodium and Potassium.- The weighed mixed chlorides were converted into chloroplatinates by solution in water and the addition of chloroplatinic acid containing 0.05 g. of Pt. per cubic centimeter.

About 0.50 c.c. was added in excess of the quantity required

to convert the chlorides into chloroplatinates on the assumption that they consist entirely of sodium chloride. The solution was then evaporated on a slow water bath (the dish being protected from direct contact with steam by a sheet of paper) until the odor of hydrochloric acid was not preceptible upon stirring the residue with a blunt glass rod. The residue was then cooled and the extraction of the sodium chloroplatinate and chloroplatinic acid effected with methyl alcohol (18).

The potassium chloroplatinate, $K_2PtCl_6$, was dried in an electric oven at 160° for two hours and from its weight the weight of potassium chloride, KCl, was found by using the conversion factor 0.3056.

## IV. EXPERIMENTAL DATA.

The data obtained in this investigation are recorded in the following tables. Unless otherwise stated, the figures in the first column in each table refer to the number of the experiment; the second column indicates the amalgam used at the start; the third, fourth and fifth columns contain the data in grams obtained by the analysis of the amalgam after the establishment of equilibrium between it and a solution of the composition as given at the top of the table. Thus column three gives the weight of the mixed alkali chlorides; column four the weight of potassium chloroplatinate, $K_2PtCl_6$; obtained in the analysis of the mixed chlorides; and column five the weight of the mercury in the equilibrium amalgam. Column six shows the concentration of the equilibrium amalgam in total milli-equivalents of amalgamated metals per 10 grams of mercury, as calculated from the data in columns three, four, and five; columns seven and eight give the mol fractions of the amalgamated metals in the amalgam at equilibrium, as calculated from columns three and four; and column nine gives the value of the expression

$$\frac{(K_{Hg})\,(NaX)}{(Na_{Hg})(KX)} = n\,k = C_c,$$

in which $(K_{Hg})$ and $(Na_{Hg})$ are the respective mol fractions in the mercurial phase, from columns seven and eight, and $(NaX)$ and $(KX)$ are the known mol fractions of the halides in the aqueous phase.

1. <u>Effect of Varying the Concentration of the Mercurial</u>

Phase at a Fixed (Equivalent) Salt-Concentration Ratio and a Fixed Normal Concentration of the Aqueous Phase.- In the sodium-potassium equilibrium, the sodium - strontium equilibrium, and also the potassium-strontium equilibrium, it has previously been observed that the total concentration of the mercurial phase exerts a marked effect on the equilibrium value, $C_c$. In the case of the sodium-strontium equilibrium the $C_c$ value was found to be a linear function of the amalgam concentration (16). In the potassium-strontium equilibrium it was found that the $C_c$ value increases directly with the amalgam concentration up to about 0.3 milli-equivalent of metals per 10 grams of mercury. In all three equilibria studied it has been observed that when highly concentrated amalgams are used the value of $C_c$ obtained are apt to be non-concordant (1).

When it was first found that the concentration of the liquid amalgams was a factor of moment, a series of determinations was carried out in which the original amalgams were diluted with varying amounts of mercury and then brought to equilibrium at 25°, with a 0.2 N equivalent mixture of sodium and potassium chloride (18). However, owing to the incompleteness of the data obtained in this series, it seemed advisable to further investigate this question.

The data for this study are given in Table 1. In this series of experiments, with equivalent sodium and potassium chloride mixtures at a total concentration of 0.20 N, the concentration of the amalgams was decreased in each successive run. It is to be noted that the mean values of the "equilibrium expression",

# TABLE I

Showing the Effect of Varying the Concentration of the Mercurial Phase at a Fixed (Equivalent) Salt - Concentration Ratio.

MIXED AQUEOUS PHASE 0.20N NaCl:KCl

TEMPERATURE 25°C

| No. | Amal. at Start | Analysis of the Equilibrium Amalgam | | | Milli-equiv. of metals per 10 g. Hg. | Mol Fractions of amalgamated metals | | |
|---|---|---|---|---|---|---|---|---|
| | | NaCl+ KCl | $K_2PtCl_6$ | Hg | | Na | K | $C_c$ |
| 1 | Na | .2118 | .2353 | 57.3 | .5858 | .7127 | .2873 | .403 |
| 2 | Na | .1860 | .2090 | 50.7 | .5810 | .7087 | .2913 | .411 |
| 3 | Na | .2180 | .2407 | 57.6 | .6004 | .7146 | .2854 | .397 |
| 4 | K | .2091 | .2300 | 55.2 | .6009 | .7154 | .2846 | .398 |
| 5 | K | .2137 | .2368 | 56.3 | .6017 | .7134 | .2866 | .401 |
| 6 | K | .1915 | .2111 | 51.0 | .5956 | .7152 | .2848 | .398 |
| | | | | Mean | .5942 | | | .401 |
| 7 | Na | .2018 | .2367 | 109.5 | .2909 | .6952 | .3048 | .438 |
| 8 | Na | .2055 | .2403 | 107.7 | .3012 | .6965 | .3035 | .435 |
| 9 | Na | .2181 | .2544 | 113.2 | .3042 | .6978 | .3022 | .433 |
| 10 | K | .2148 | .2515 | 115.9 | .2848 | .6962 | .3038 | .436 |
| 11 | K | .2299 | .2698 | 118.1 | .3066 | .6948 | .3052 | .439 |
| 12 | K | .2133 | .2491 | 108.8 | .3094 | .6968 | .3032 | .435 |
| | | | | Mean | .2995 | | | .436 |
| 13 | Na | .1843 | .2210 | 198.2 | .1465 | .6881 | .3119 | .453 |
| 14 | Na | .1990 | .2379 | 197.4 | .1588 | .6890 | .3110 | .451 |
| 15 | Na | .2068 | .2476 | 197.4 | .1650 | .6888 | .3112 | .451 |
| 16 | K | .2240 | .2720 | 199.0 | .1771 | .6838 | .3162 | .462 |
| 17 | K | .2265 | .2715 | 201.0 | .1775 | .6879 | .3121 | .453 |
| 18 | K | .2310 | .2773 | 199.6 | .1824 | .6880 | .3120 | .453 |
| | | | | Mean | .1679 | | | .454 |
| 19 | Na | .2091 | .2551 | 261.8 | .1263 | .6839 | .3161 | .462 |
| 20 | Na | .1650 | .1957 | 256.8 | .1013 | .6917 | .3083 | .445 |
| 21 | Na | .1575 | .1868 | 261.2 | .0950 | .6887 | .3113 | .452 |
| 22 | K | .2176 | .2648 | 262.9 | .1302 | .6850 | .3150 | .459 |
| 23 | K | .2311 | .2790 | 279.2 | .1299 | .6859 | .3141 | .457 |
| 24 | K | .1694 | .2039 | 253.6 | .1050 | .6864 | .3136 | .456 |
| | | | | Mean | .1146 | | | .455 |
| 25 | Na | .2101 | .2546 | 557.1 | .0593 | .6844 | .3156 | .461 |
| 26 | K | .2152 | .2627 | 573.5 | .0586 | .6831 | .3169 | .463 |
| 27 | K | .2033 | .2463 | 554.0 | .0573 | .6882 | .3118 | .453 |
| 28 | K | .2171 | .2594 | 560.5 | .0617 | .6873 | .3127 | .455 |
| | | | | Mean | .0592 | | | .458 |

## TABLE II.

MIXED AQUEOUS PHASE 0.50N NaCl:KCl

TEMPERATURE 25°C

| No. | Amal. at Start | Analysis of the Equilibrium Amalgam | | | Milli-equiv. of metals per 10 g. Hg. | Mol Fractions of amalgamated metals | | $C_c$ |
|---|---|---|---|---|---|---|---|---|
| | | $NaCl+KCl$ | $K_2PtCl_6$ | Hg | | Na | K | |
| 1 | Na | .2235 | .2512 | 80.5 | .4397 | .7094 | .2906 | .410 |
| 2 | Na | .2268 | .2548 | 81.8 | .4391 | .4091 | .2909 | .410 |
| 3 | Na | .2149 | .2439 | 80.0 | .4251 | .7062 | .2938 | .416 |
| 4 | K | .2067 | .2354 | 81.5 | .4012 | .7051 | .2949 | .418 |
| 5 | K | .2236 | .2523 | 80.3 | .4408 | .7078 | .2922 | .413 |
| 6 | K | .2208 | .2485 | 80.2 | .4360 | .7089 | .2911 | .410 |
| | | | | Mean | .4303 | | | .413 |
| 7 | Na | .2130 | .2506 | 197.1 | .1705 | .6941 | .3059 | .441 |
| 8 | Na | .2080 | .2439 | 196.6 | .1669 | .6956 | .3044 | .437 |
| 9 | Na | .2147 | .2519 | 198.5 | .1707 | .6952 | .3048 | .438 |
| 10 | K | .2156 | .2534 | 196.0 | .1735 | .6948 | .3052 | .439 |
| 11 | K | .2148 | .2531 | 198.1 | .1710 | .6945 | .3055 | .440 |
| 12 | K | .2219 | .2614 | 196.5 | .1781 | .6939 | .3061 | .441 |
| | | | | Mean | .1718 | | | .439 |

# TABLE III.

MIXED AQUEOUS PHASE 1.00N NaCl:KCl

TEMPERATURE 25°C

| No. | Amal. at Start | Analysis of the Equilibrium Amalgam | | | Milli-equiv. of metals per 10 g. Hg. | Mol fractions of amalgamated metals | | $C_c$ |
|---|---|---|---|---|---|---|---|---|
| | | NaCl+ KCl | $K_2PtCl_6$ | Hg | | Na | K | |
| 1 | Na | .2236 | .2414 | 67.0 | .5302 | .7213 | .2787 | .386 |
| 2 | Na | .2213 | .2389 | 66.7 | .5271 | .7215 | .2785 | .386 |
| 3 | Na | .2195 | .2404 | 76.8 | .4536 | .7170 | .2830 | .394 |
| 4 | K | .2183 | .2366 | 66.9 | .5183 | .7207 | .2793 | .387 |
| 5 | K | .2242 | .2418 | 68.0 | .5238 | .7217 | .2783 | .385 |
| 6 | K | .2276 | .2454 | 67.6 | .5349 | .7218 | .2782 | .385 |
| | | | | Mean | .5146 | | | .387 |
| 7 | Na | .2240 | .2520 | 100.4 | .3533 | .7089 | .2911 | .410 |
| 8 | Na | .2266 | .2540 | 101.2 | .3547 | .7100 | .2900 | .408 |
| 9 | Na | .2210 | .2476 | 100.5 | .3483 | .7100 | .2900 | .408 |
| 10 | K | .2254 | .2521 | 100.2 | .3564 | .7108 | .2892 | .407 |
| 11 | K | .2334 | .2612 | 102.2 | .3618 | .7105 | .2895 | .407 |
| 12 | K | .2237 | .2510 | 100.7 | .3518 | .7097 | .2903 | .409 |
| | | | | Mean | .3544 | | | .408 |
| 13 | Na | .2172 | .2496 | 197.0 | .1728 | .7019 | .2981 | .424 |
| 14 | Na | .1967 | .2272 | 187.6 | .1656 | .7005 | .2995 | .427 |
| 15 | Na | .1808 | .2091 | 193.7 | .1475 | .6997 | .3003 | .429 |
| 16 | K | .1979 | .2284 | 195.0 | .1618 | .6998 | .3002 | .429 |
| 17 | K | .1960 | .2274 | 195.1 | .1586 | .6990 | .3010 | .431 |
| 18 | K | .2203 | .2537 | 197.0 | .1767 | .7013 | .2987 | .426 |
| | | | | Mean | .1639 | | | .427 |

## TABLE IV.

MIXED AQUEOUS PHASE 2.00N NaCl:KCl

TEMPERATURE 25°C

| No. | Amal. at Start | Analysis of the Equilibrium Amalgam | | | Milli-equiv. of metals per 10 g. Hg. | Mol Fractions of Amalgamated Metals | | $C_c$ |
|---|---|---|---|---|---|---|---|---|
| | | NaCl+ KCl | $K_2PtCl_6$ | Hg | | Na | K | |
| 1 | Na | .2307 | .2369 | 67.6 | .5442 | .7364 | .2636 | .358 |
| 2 | Na | .2320 | .2389 | 68.5 | .5400 | .7357 | .2643 | .359 |
| 3 | Na | .2219 | .2277 | 66.9 | .5289 | .7333 | .2667 | .364 |
| 4 | K | .2276 | .2355 | 67.1 | .5406 | .7337 | .2663 | .363 |
| 5 | K | .2310 | .2371 | 67.4 | .5466 | .7364 | .2636 | .358 |
| 6 | K | .2297 | .2366 | 68.3 | .5362 | .7352 | .2648 | .360 |
| | | | | Mean | .5394 | | | .360 |
| 7 | Na | .2284 | .2413 | 100.5 | .3616 | .7280 | .2720 | .373 |
| 8 | Na | .2304 | .2438 | 100.6 | .3644 | .7274 | .2726 | .374 |
| 9 | Na | .2280 | .2407 | 101.0 | .3592 | .7279 | .2721 | .373 |
| 10 | K | .2345 | .2454 | 100.2 | .3726 | .7306 | .2694 | .369 |
| 11 | K | .2355 | .2491 | 100.3 | .3739 | .7276 | .2724 | .374 |
| 12 | K | .2376 | .2506 | 101.2 | .3736 | .7283 | .2717 | .373 |
| | | | | Mean | .3675 | | | .373 |
| 13 | Na | .1238 | .1393 | 190.0 | .1032 | .7080 | .2920 | .412 |
| 14 | Na | .1654 | .1842 | 188.5 | .1347 | .7125 | .2875 | .403 |
| 15 | K | .2164 | .2406 | 200.0 | .1700 | .7189 | .2811 | .391 |
| 16 | K | .2046 | .2268 | 198.8 | .1631 | .7138 | .2862 | .400 |
| 17 | K | .1772 | .1969 | 199.4 | .1453 | .7125 | .2875 | .403 |
| | | | | Mean | .1432 | | | .402 |

# TABLE V.

MIXED AQUEOUS PHASE 4.00N NaCl:KCl

TEMPERATURE 25°C

| No. | Amal. at Start | Analysis of the Equilibrium Amalgam | | | Milli-equiv. of metals per 10 g. Hg. | Mol Fractions of Amalgamated Metals | | $C_c$ |
|---|---|---|---|---|---|---|---|---|
| | | NaCl+ KCl | $K_2PtCl_6$ | Hg | | Na | K | |
| 1 | Na | .2060 | .1939 | 80.8 | .4089 | .7593 | .2407 | .317 |
| 2 | Na | .2076 | .1969 | 80.7 | .4124 | .7575 | .2425 | .320 |
| 3 | Na | .2085 | .1997 | 80.6 | .4145 | .7551 | .2449 | .324 |
| 4 | K | .2152 | .2046 | 81.3 | .4219 | .7574 | .2426 | .320 |
| 5 | K | .2154 | .2062 | 82.0 | .4257 | .7552 | .2448 | .324 |
| 6 | K | .2081 | .1980 | 80.8 | .4116 | .7563 | .2437 | .322 |
| | | | | Mean | .4159 | | | .321 |
| 7 | Na | .2314 | .2307 | 200.0 | .1849 | .7443 | .2557 | .343 |
| 8 | Na | .2148 | .2119 | 197.8 | .1736 | .7468 | .2532 | .339 |
| 9 | Na | .2179 | .2184 | 199.1 | .1748 | .7430 | .2570 | .346 |
| 10 | K | .2014 | .2014 | 196.6 | .1635 | .7434 | .2566 | .345 |
| 11 | K | .2068 | .2033 | 197.3 | .1669 | .7488 | .2512 | .335 |
| 12 | K | .2333 | .2286 | 199.8 | .1866 | .7450 | .2550 | .342 |
| | | | | Mean | .1750 | | | .342 |

$C_c$, obtained in the different runs increase with decreasing amalgam concentration. In any one run, the equilibrium amalgams of the individual mixtures were always found to differ somewhat in concentration; because in the first place, the stock amalgams were weighed out more or less roughly for dilution, and, in the second place evolution of hydrogen (always in evidence to a very slight extent, at best) varied somewhat in the individual experiment. However, the individual values of $C_c$ do not differ enough for these slight changes of amalgam concentration in the individual experiments of a run to warrant a correction as in the case of the sodium-strontium equilibrium (16), or of the potassium-strontium equilibrium (17).

Tables II, III, IV and V contain data showing the effect of varying the amalgam concentration, but with equivalent sodium and potassium chloride mixtures of 0.50, 1.00, 2.00 and 4.00 normal concentrations, respectively.

In Figure 1, the values of $C_c$ as ordinates, are plotted against the total amalgam concentration in milli-equivalents of metals per 10 grams of mercury. Each point indicated in the plot is the average of about six separate determinations.

### 2. Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed (Equivalent) Salt-Concentration Ratio and at Various Specific Amalgam Concentrations.-

Table VI contains data showing the effect of increasing the total salt concentration in stages from 0.20 N to 4.00 N the salts (sodium and potassium chlorides) being present in equivalent proportions- at various fixed amalgam concentrations. The values of $C_c$ in this table were

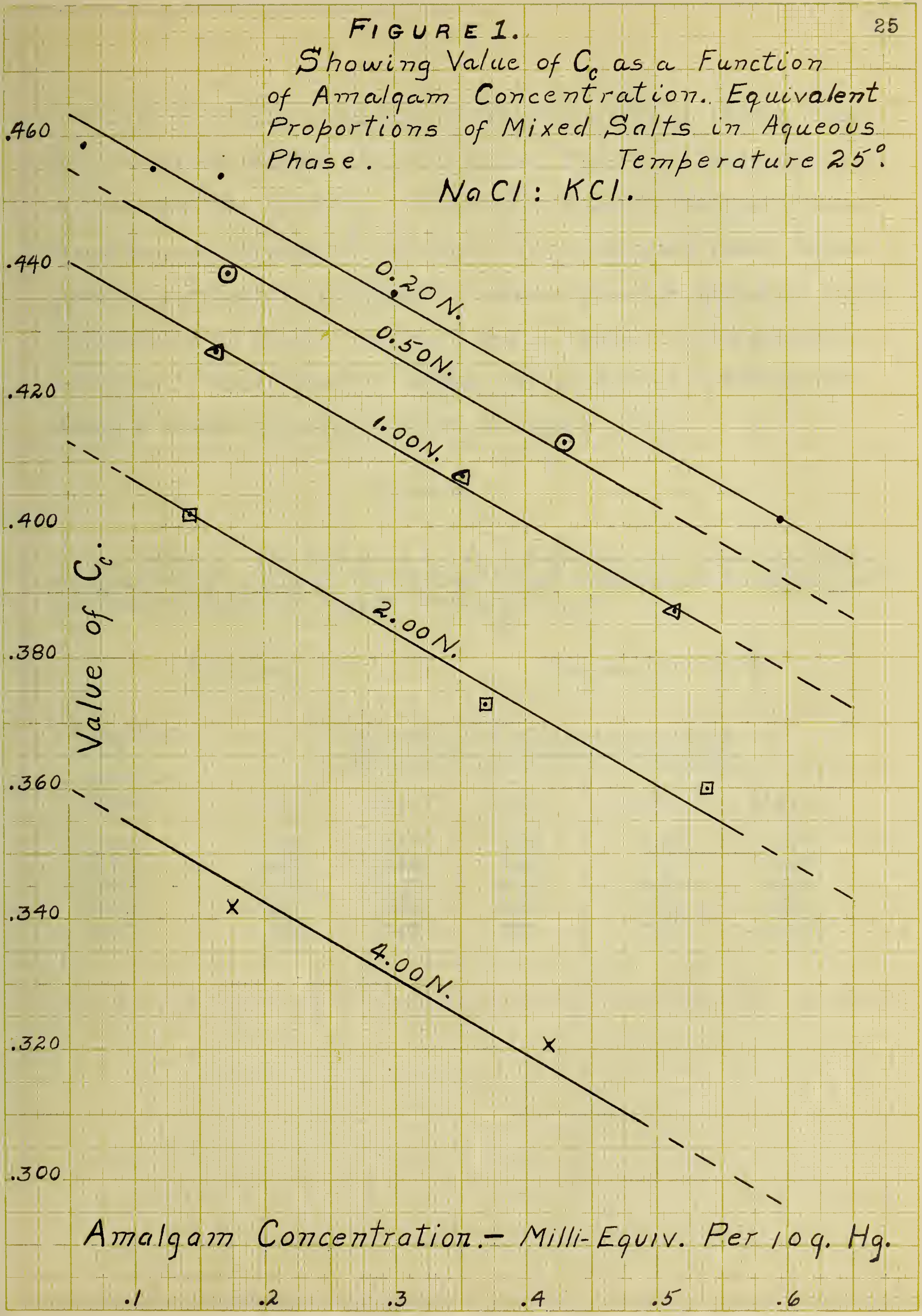


FIGURE 1.
Showing Value of $C_c$ as a Function of Amalgam Concentration. Equivalent Proportions of Mixed Salts in Aqueous Phase. Temperature 25°.
NaCl : KCl.

obtained by simply reading them from the plots in Figure 1, at the indicated amalgam concentrations. Figure 2 illustrates the effect upon the $C_c$ value, at different specific amalgam concentrations, of varying the normality of the aqueous phase in the case of equivalent sodium and potassium chloride mixtures. From this series of plots it appears that a change in concentration of 0.1 milli-equivalent of metals per 10 grams of mercury produces a change of about .012 in the value of $C_c$.

## TABLE VI.

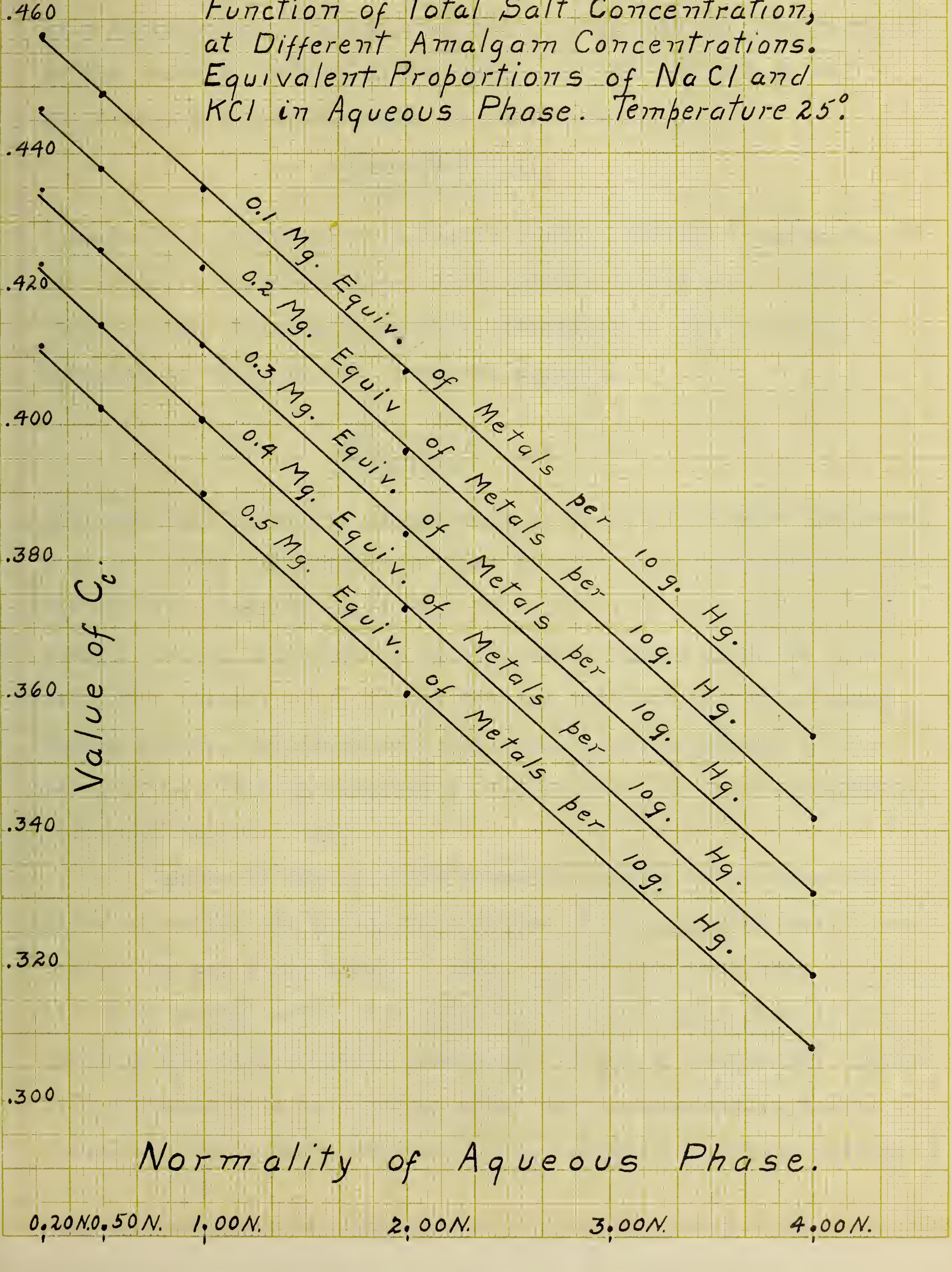
Showing the Value of $C_c$ as a Function of Total Salt Concentration at a Fixed (Equivalent) Salt-Concentration Ratio and at Various Specific Amalgam Concentrations.

NaCl:KCl Temperature 25°C.

| Normality of aqueous phase | $C_c$ values at x milli-equivalents of metals per 10 grams of mercury. | | | | |
|---|---|---|---|---|---|
| | x=0.1 | x=0.2 | x=0.3 | x=0.4 | x=0.5 |
| 0.20 | .458 | .447 | .435 | .424 | .412 |
| 0.50 | .449 | .438 | .426 | .415 | .403 |
| 1.00 | .435 | .423 | .412 | .401 | .389 |
| 2.00 | .408 | .396 | .384 | .373 | .360 |
| 4.00 | .354 | .342 | .331 | .319 | .308 |

FIGURE 2.

Showing Value of $C_c$ as a Function of Total Salt Concentration, at Different Amalgam Concentrations. Equivalent Proportions of NaCl and KCl in Aqueous Phase. Temperature 25°.



3. Effect of Varying the Concentration Ratio of the Salts at a Fixed Normal Concentration and a Fixed Amalgam Concentration.- If the reaction between alkali metal amalgams and alkali salt solutions is ionic, the mass law expression,

$$\frac{(K_{Hg})(Na+)}{(Na_{Hg})(K+)} = k,$$

demands that the value of k should remain constant, regardless of the relative concentrations of the simple sodium and potassium ions; on the other hand, however, constancy is not necessarily demanded in the value of $C_c$ in the equation

$$\frac{(K_{Hg})(NaX)}{(Na_{Hg})(KX)} = n\ k = C_c .$$

The results of previous experiments carried out in this laboratory with undiluted amalgams show "that if the total concentration of the solution remains constant, the value of $C_c$ is constant even though the mol fractions of the two salts in the mixtures vary over wide limits..... . When diluted amalgams and more concentrated aqueous solutions were employed, a slight change in the value of $C_c$ could be observed as the ratio of the salt concentrations was varied." (18).

Table VII contains the results obtained by varying the ratio of sodium and potassium chloride solutions whose total concentration was 0.20 normal. These experiments show that within the experimental error, the value of $C_c$ is constant when dilute amalgams and rather dilute aqueous solutions are employed. Table VIII contains data at a higher total salt concentration (1.00 normal). While there appears to be a slight difference between the

## TABLE VII

Showing the Effect of Varying the Concentration Ratio of the Salts at a Fixed Normal Concentration and a Fixed Amalgam Concentration.

MIXED AQUEOUS PHASE 0.20N. TEMPERATURE 25°C.

| No. | Amal. at start | Analysis of the equilibrium amalgam |  |  | Milli-equiv. of metals per 10 g. Hg. | Mol fractions of amalgamated metals |  | $C_c$ |
|---|---|---|---|---|---|---|---|---|
|  |  | NaCl+ KCl | $K_2PtCl_6$ | Hg |  | Na | K |  |
|  |  |  |  | 2 NaCl : KCl |  |  |  |  |
| 1 | Na | .2191 | .1603 | 201.1 | .1773 | .8157 | .1843 | .452 |
| 2 | Na | .2116 | .1544 | 202.3 | .1703 | .8162 | .1838 | .450 |
| 3 | Na | .2180 | .1600 | 200.3 | .1771 | .8152 | .1848 | .453 |
| 4 | K | .2200 | .1615 | 201.5 | .1777 | .8153 | .1847 | .453 |
| 5 | K | .2190 | .1607 | 200.3 | .1779 | .8152 | .1848 | .453 |
| 6 | K | .2124 | .1553 | 200.6 | .1724 | .8155 | .1845 | .452 |
|  |  |  |  | Mean | .1754 |  |  | .452 |
|  |  |  |  | NaCl : KCl |  |  |  |  |
| (See Table I. Nos. 13-18) |  |  |  | Mean | .1679 |  |  | .454 |
|  |  |  |  | NaCl : 2 KCl |  |  |  |  |
| 7 | Na | .2321 | .4062 | 201.6 | .1741 | .5260 | .4740 | .451 |
| 8 | Na | .2279 | .3988 | 200.2 | .1722 | .5258 | .4742 | .451 |
| 9 | Na | .2227 | .3900 | 201.1 | .1678 | .5255 | .4745 | .451 |
| 10 | K | .2321 | .4091 | 200.6 | .1749 | .5222 | .4778 | .457 |
| 11 | K | .2329 | .4101 | 200.6 | .1755 | .5224 | .4776 | .457 |
| 12 | K | .2352 | .4139 | 202.8 | .1753 | .5229 | .4771 | .456 |
|  |  |  |  | Mean | .1733 |  |  | .454 |

# TABLE VIII

Showing the Effect of Varying the Concentration Ratio of the Salts at a Fixed Normal Concentration and a Fixed Amalgam Concentration.

MIXED AQUEOUS PHASE 1.00 N. TEMPERATURE 25°C.

2 NaCl : KCl

| No. | Amal. at start | Analysis of the equilibrium amalgam | | | Milli-equiv. of metals per 10 g. Hg. | Mol fractions of amalgamated metals | | $C_c$ |
|---|---|---|---|---|---|---|---|---|
| | | NaCl+ KCl | $K_2PtCl_6$ | Hg | | Na | K | |
| 1 | Na | .2221 | .1546 | 201.4 | .1800 | .8253 | .1747 | .424 |
| 2 | Na | .2173 | .1544 | 201.5 | .1748 | .8203 | .1797 | .438 |
| 3 | K | .2194 | .1577 | 201.2 | .1776 | .8192 | .1808 | .440 |
| 4 | K | .2297 | .1608 | 203.8 | .1839 | .8243 | .1757 | .426 |
| 5 | K | .2120 | .1528 | 201.0 | .1718 | .8187 | .1813 | .442 |
| | | | | Mean | .1776 | | | .434 |

NaCl: KCl

| | | |
|---|---|---|
| (See Table III.Nos. 13-18) Mean | .1639 | .427 |

values of $C_c$ obtained with equivalent proportions of sodium and potassium chloride and those obtained with a ratio of 2NaCl:KCl, this difference falls within the limit of accuracy of the latter run. These results are in accordance with those previously obtained.

4. Effect of Varying the Normal Concentration of Equivalent Sodium and Potassium Chloride, Bromide, or Iodide Mixtures at a Fixed Amalgam Concentration.- In a previous study of the effect of increasing the total salt concentration in sodium and potassium chloride mixtures, at a fixed salt-concentration ratio, it was found (25) that upon raising the salt concentration the value of the equilibrium expression, $C_c$, decreased. This study was later extended and now includes mixtures of sodium and potassium sulfates and chlorides (18), strontium and sodium chlorides (16), and strontium and potassium chlorides (17). It seemed advisable to continue this investigation in the case of equivalent solutions of sodium and potassium chlorides, bromides and iodides.

The data for this study are given in Tables IX, X, XI, XII, XIII and XIV. The total concentration of the equivalent mixtures was increased from 0.10 normal to 4.00 normal for each salt mixture, with the exception of the sodium bromide - potassium iodide and sodium iodide - potassium iodide mixtures with which the concentration was increased from 0.20 normal to 4.00 normal. In all of the individual experiments of each run the amalgams were diluted to the same approximate concentration (about 0.2 milliequivalents of metal per 10 grams of mercury). While the final concentration of the equilibrium amalgam was slightly less than

## TABLE IX.

Showing the Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed (Equivalent) Salt-Concentration Ratio.

MIXED AQUEOUS PHASE 0.10 N. NaCl:KCl.

TEMPERATURE 25°C.

| No. | Amal. at start | Analysis of the equilibrium amalgam | | | Milli-equiv. of metals per 10 g. Hg. | Mol fractions of amalgamated metals | | $C_c$ |
|---|---|---|---|---|---|---|---|---|
| | | NaCl+ KCl | $K_2PtCl_6$ | Hg. | | Na | K | |
| 1 | Na | .1860 | .2223 | 197.9 | .1481 | .6892 | .3108 | .451 |
| 2 | Na | .1638 | .1959 | 193.4 | .1334 | .6886 | .3114 | .452 |
| 3 | K | .1872 | .2241 | 197.2 | .1500 | .6895 | .3105 | .450 |
| 4 | K | .1798 | .2165 | 194.3 | .1499 | .6844 | .3156 | .461 |
| 5 | K | .1949 | .2322 | 199.0 | .1544 | .6897 | .3103 | .450 |
| | | | | Mean | .1472 | | | .453 |
| MIXED AQUEOUS PHASE 0.20 N. | | | | | | NaCl:KCl. | | |
| (See Table I. Nos. 13-18) | | | | Mean | .1679 | | | .454 |
| MIXED AQUEOUS PHASE 0.50 N. | | | | | | NaCl:KCl. | | |
| (See Table II.Nos. 7-12) | | | | Mean | .1718 | | | .439 |
| MIXED AQUEOUS PHASE 1.00 N. | | | | | | NaCl:KCl. | | |
| (See Table III.Nos. 13-18) | | | | Mean | .1639 | | | .427 |
| MIXED AQUEOUS PHASE 1.983 N.* | | | | | | .983 NaCl:KCl. | | |
| 6 | Na | .2015 | .2259 | 197.4 | .1616 | .7100 | .2900 | .401 |
| 7 | Na | .2073 | .2324 | 200.2 | .1645 | .7100 | .2900 | .401 |
| 8 | Na | .2223 | .2491 | 198.0 | .1727 | .7101 | .2899 | .401 |
| 9 | K | .2217 | .2520 | 201.3 | .1700 | .7056 | .2944 | .410 |
| 10 | K | .2201 | .2458 | 200.6 | .1738 | .7112 | .2888 | .399 |
| 11 | K | .2185 | .2446 | 200.0 | .1731 | .7106 | .2894 | .400 |
| | | | | Mean | .1693 | | | .402 |
| MIXED AQUEOUS PHASE 2.00 N | | | | | | NaCl:KCl. | | |
| (See Table IV. Nos.13-17) | | | | Mean | .1432 | | | .402 |

## TABLE IX. (continued)

Showing the Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed (Equivalent) Salt-Concentration Ratio.

MIXED AQUEOUS PHASE 4.00 N. NaCl:KCl

TEMPERATURE 25°C.

| No. | Amal. at start. | Analysis of the equilibrium amalgam | | | Milli-equiv. of metals per 10 g. Hg. | Mol fractions of amalgamated metals | | $C_c$ |
|---|---|---|---|---|---|---|---|---|
| | | NaCl+ KCl | $K_2PtCl_6$ | Hg. | | Na | K | |
| (See Table V. Nos. 7-12) | | | | Mean | .1750 | | | .342 |

*It should be noted that the normality ratios for Experiments 6-11 of Table IX are 0.983 NaCl to 1.000 KCl instead of 1.000 and 1.000 as was intended. This error in making up the NaCl solution was not detected until the run had been completed. The values of 0.983 N. NaCl and 1.000 N. KCl were used in calculating $C_c$. (Table IV, Nos. 13-17, gives the run as repeated at a total 2.000 normal concentration).

## TABLE X.

Showing the Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed (Equivalent) Salt-Concentration Ratio.

MIXED AQUEOUS PHASE 0.10 N. NaCl:KBr.

TEMPERATURE 25°C.

| No. | Amal. at start | Analysis of the equilibrium amalgam | | | Milli-equiv. of metals per 10 g. Hg. | Mol fractions of amalgamated metals | | $C_c$ |
|---|---|---|---|---|---|---|---|---|
| | | NaCl+ KCl | $K_2PtCl_6$ | Hg. | | Na | K | |
| 1 | Na | .2065 | .2504 | 200.2 | .1615 | .6828 | .3172 | .465 |
| 2 | Na | .1870 | .2268 | 200.7 | .1465 | .6810 | .3190 | .468 |
| 3 | Na | .1847 | .2247 | 199.4 | .1457 | .6829 | .3171 | .465 |
| 4 | K | .2022 | .2458 | 199.4 | .1595 | .6834 | .3166 | .461 |
| 5 | K | .2080 | .2465 | 200.6 | .1635 | .6921 | .3079 | .444 |
| 6 | K | .2055 | .2489 | 202.0 | .1601 | .6845 | .3155 | .461 |
| | | | | Mean | .1561 | | | .461 |
| | | MIXED AQUEOUS PHASE 0. 20 N. | | | | NaCl:KBr. | | |
| 7 | Na | .2260 | .2726 | 198.8 | .1790 | .6864 | .3136 | .457 |
| 8 | Na | .2308 | .2776 | 201.8 | .1801 | .6887 | .3113 | .452 |
| 9 | Na | .2180 | .2584 | 200.8 | .1711 | .6917 | .3083 | .445 |
| 10 | K | .2269 | .2749 | 200.7 | .1779 | .6845 | .3155 | .460 |
| 11 | K | .2210 | .2662 | 198.6 | .1754 | .6859 | .3141 | .457 |
| 12 | K | .2205 | .2636 | 200.8 | .1730 | .6889 | .3111 | .450 |
| | | | | Mean | .1761 | | | .453 |
| | | MIXED AQUEOUS PHASE 0.50 N. | | | | NaCl:KBr. | | |
| 13 | Na | .2436 | .2894 | 210.9 | .1821 | .6912 | .3088 | .446 |
| 14 | Na | .2328 | .2753 | 202.0 | .1817 | .6928 | .3072 | .443 |
| 15 | Na | .2254 | .2676 | 201.0 | .1768 | .6912 | .3088 | .446 |
| 16 | K | .2315 | .2741 | 201.1 | .1815 | .6923 | .3077 | .444 |
| 17 | K | .2246 | .2656 | 199.1 | .1779 | .6922 | .3078 | .444 |
| 18 | K | .2268 | .2682 | 200.2 | .1791 | .6906 | .3094 | .448 |
| | | | | Mean | .1798 | | | .445 |

## TABLE X (continued)

Showing the Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed (Equivalent) Salt-Concentration Ratio.

MIXED AQUEOUS PHASE 1.00 N. NaCl:KBr.

TEMPERATURE 25°C.

| No. | Amal. at start | Analysis of the equilibrium amalgam | | | Milli-equiv. of metals 10 g. Hg. | Mol fractions of amalgamated metals | | $C_c$ |
|---|---|---|---|---|---|---|---|---|
| | | NaCl+ KCl | $K_2PtCl_6$ | Hg. | | Na | K | |
| 19 | Na | .2293 | .2654 | 201.2 | .1800 | .6998 | .3002 | .429 |
| 20 | Na | .2314 | .2687 | 200.8 | .1819 | .6987 | .3013 | .431 |
| 21 | Na | .2238 | .2596 | 200.5 | .1763 | .6991 | .3009 | .430 |
| 22 | K | .2244 | .2614 | 201.0 | .1762 | .6976 | .3024 | .433 |
| 23 | K | .2316 | .2666 | 200.0 | .1830 | .7014 | .2986 | .426 |
| 24 | K | .2272 | .2624 | 200.4 | .1791 | .7004 | .2996 | .428 |
| 25 | Na | .2275 | .2607 | 200.8 | .1791 | .7028 | .2972 | .423 |
| 26 | Na | .2287 | .2600 | 201.0 | .1800 | .7053 | .2947 | .418 |
| 27 | Na | .2184 | .2500 | 200.0 | .1727 | .7033 | .2967 | .422 |
| 28 | K | .2348 | .2688 | 201.5 | .1842 | .7036 | .2964 | .421 |
| 29 | K | .2174 | .2491 | 192.4 | .1786 | .7031 | .2969 | .422 |
| 30 | K | .2208 | .2519 | 201.0 | .1737 | .7043 | .2957 | .420 |
| | | | | Mean | .1762 | | | .425 |

MIXED AQUEOUS PHASE 2.00 N. NaCl:KBr.

| No. | Amal. at start | NaCl+ KCl | $K_2PtCl_6$ | Hg. | Milli-equiv. of metals 10 g. Hg. | Na | K | $C_c$ |
|---|---|---|---|---|---|---|---|---|
| 31 | Na | .2351 | .2575 | 199.6 | .1869 | .7171 | .2829 | .394 |
| 32 | Na | .2372 | .2625 | 199.3 | .1887 | .7142 | .2858 | .400 |
| 33 | K | .2492 | .2734 | 205.6 | .1922 | .7165 | .2835 | .395 |
| 34 | K | .2410 | .2633 | 202.0 | .1896 | .7170 | .2830 | .394 |
| 35 | K | .2437 | .2672 | 202.7 | .1907 | .7170 | .2830 | .394 |
| | | | | Mean | .1896 | | | .395 |

MIXED AQUEOUS PHASE 4.00 N. NaCl:KBr.

| No. | Amal. at start | NaCl+ KCl | $K_2PtCl_6$ | Hg. | Milli-equiv. of metals 10 g. Hg. | Na | K | $C_c$ |
|---|---|---|---|---|---|---|---|---|
| 36 | Na | .2470 | .2366 | 202.0 | .1959 | .7550 | .2450 | .324 |
| 37 | Na | .2332 | .2340 | 200.0 | .1869 | .7435 | .2565 | .344 |
| 38 | Na | .2446 | .2375 | 201.5 | .1943 | .7513 | .2487 | .330 |
| 39 | K | .2372 | .2283 | 200.8 | .1892 | .7536 | .2464 | .327 |
| 40 | K | .2355 | .2253 | 200.8 | .1879 | .7555 | .2445 | .324 |
| 41 | K | .2328 | .2270 | 200.5 | .1857 | .7494 | .2506 | .334 |
| | | | | Mean | .1898 | | | .330 |

## TABLE XI.

Showing the Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed (Equivalent) Salt-Concentration Ratio.

MIXED AQUEOUS PHASE 0.10 N. NaCl:KI.

TEMPERATURE 25°C.

| No. | Amal. at start | Analysis of the equilibrium amalgam | | | Milli-equiv. of metals per 10 g. Hg. | Mol fractions of amalgamated metals | | $C_c$ |
|---|---|---|---|---|---|---|---|---|
| | | NaCl+ KCl | $K_2PtCl_6$ | Hg. | | Na | K | |
| 1 | Na | .2081 | .2510 | 197.6 | .1657 | .6860 | .3140 | .457 |
| 2 | Na | .1919 | .2337 | 198.4 | .1521 | .6828 | .3172 | .465 |
| 3 | Na | .2091 | .2536 | 200.0 | .1645 | .6859 | .3141 | .457 |
| 4 | K | .2040 | .2455 | 200.0 | .1606 | .6864 | .3136 | .456 |
| 5 | K | .2050 | .2466 | 191.1 | .1608 | .6869 | .3131 | .455 |
| 6 | K | .2154 | .2574 | 199.5 | .1701 | .6898 | .3102 | .449 |
| 7 | Na | .1950 | .2362 | 198.3 | .1547 | .6844 | .3156 | .461 |
| 8 | Na | .1966 | .2370 | 194.4 | .1592 | .6863 | .3137 | .457 |
| 9 | Na | .2003 | .2399 | 200.3 | .1575 | .6885 | .3115 | .452 |
| 10 | K | .1931 | .2332 | 198.1 | .1535 | .6859 | .3141 | .458 |
| 11 | K | .1955 | .2371 | 198.3 | .1551 | .6844 | .3156 | .461 |
| 12 | K | .2033 | .2460 | 198.7 | .1600 | .6847 | .3153 | .460 |
| | | | | Mean | .1595 | | | .457 |

MIXED AQUEOUS PHASE 0.20 N. NaCl:KI.

| No. | Amal. at start | NaCl+ KCl | $K_2PtCl_6$ | Hg. | Milli-equiv. of metals per 10 g. Hg. | Na | K | $C_c$ |
|---|---|---|---|---|---|---|---|---|
| 13 | Na | .2166 | .2640 | 199.7 | .1706 | .6823 | .3178 | .465 |
| 14 | Na | .2208 | .2641 | 200.7 | .1733 | .6889 | .3111 | .451 |
| 15 | Na | .2145 | .2556 | 199.2 | .1697 | .6902 | .3098 | .448 |
| 16 | K | .2173 | .2598 | 189.5 | .1753 | .6900 | .3100 | .449 |
| 17 | K | .2256 | .2681 | 198.1 | .1794 | .6906 | .3094 | .448 |
| | | | | Mean | .1736 | | | .452 |

MIXED AQUEOUS PHASE 0.50 N. NaCl:KI.

| No. | Amal. at start | NaCl+ KCl | $K_2PtCl_6$ | Hg. | Milli-equiv. of metals per 10 g. Hg. | Na | K | $C_c$ |
|---|---|---|---|---|---|---|---|---|
| 18 | Na | .2211 | .2568 | 198.8 | .1712 | .7012 | .2988 | .426 |
| 19 | Na | .2206 | .2548 | 198.7 | .1709 | .7007 | .2993 | .427 |
| 20 | Na | .2203 | .2547 | 197.8 | .1759 | .7002 | .2998 | .428 |
| 21 | K | .2141 | .2490 | 200.4 | .1687 | .6981 | .3019 | .432 |
| 22 | K | .2177 | .2529 | 203.0 | .1693 | .6985 | .3015 | .431 |
| 23 | K | .2150 | .2486 | 196.3 | .1728 | .6956 | .3044 | .437 |
| | | | | Mean | .1748 | | | .430 |

TABLE XI. (continued)

Showing the Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed (Equivalent) Salt-Concentration Ratio.

MIXED AQUEOUS PHASE 1.00 N. NaCl:KI.

TEMPERATURE 25°C.

| No. | Amal. at start | Analysis of the equilibrium amalgam | | | Milli-equiv. of metals per 10 g. Hg. | Mol fractions of amalgamated metals | | $C_c$ |
|---|---|---|---|---|---|---|---|---|
| | | NaCl+ KCl | $K_2PtCl_6$ | Hg. | | Na | K | |
| 24 | Na | .2260 | .2530 | 199.2 | .1797 | .7104 | .2896 | .407 |
| 25 | Na | .2228 | .2500 | 196.5 | .1752 | .7096 | .2904 | .409 |
| 26 | Na | .2265 | .2541 | 200.0 | .1785 | .7099 | .2901 | .408 |
| 27 | K | .2195 | .2472 | 201.0 | .1728 | .7077 | .2923 | .413 |
| 28 | K | .2232 | .2492 | 201.0 | .1759 | .7114 | .2886 | .405 |
| 29 | K | .2200 | .2460 | 198.4 | .1755 | .7081 | .2919 | .412 |
| | | | | Mean | .1763 | | | .409 |

MIXED AQUEOUS PHASE 2.00 N. NaCl:KI.

| No. | Amal. at start | NaCl+ KCl | $K_2PtCl_6$ | Hg. | Milli-equiv. of metals per 10 g. Hg. | Na | K | $C_c$ |
|---|---|---|---|---|---|---|---|---|
| 30 | Na | .2381 | .2492 | 202.0 | .1879 | .7311 | .2689 | .367 |
| 31 | Na | .2333 | .2437 | 200.3 | .1856 | .7317 | .2683 | .366 |
| 32 | Na | .2325 | .2392 | 198.8 | .1876 | .7357 | .2643 | .358 |
| 33 | K | .2184 | .2269 | 201.1 | .1730 | .7329 | .2671 | .364 |
| 34 | K | .2245 | .2346 | 201.2 | .1776 | .7310 | .2690 | .367 |
| 35 | K | .2339 | .2425 | 200.5 | .1860 | .7336 | .2664 | .363 |
| | | | | Mean | .1829 | | | .365 |

MIXED AQUEOUS PHASE 4.00 N. NaCl:KI.

| No. | Amal. at start | NaCl+ KCl | $K_2PtCl_6$ | Hg. | Milli-equiv. of metals per 10 g. Hg. | Na | K | $C_c$ |
|---|---|---|---|---|---|---|---|---|
| 36 | Na | .2266 | .2002 | 197.0 | .1853 | .7751 | .2249 | .290 |
| 37 | Na | .2369 | .2144 | 201.5 | .1891 | .7695 | .2305 | .299 |
| 38 | Na | .2342 | .2069 | 200.2 | .1884 | .7753 | .2247 | .290 |
| 39 | K | .2305 | .2108 | 198.9 | .1860 | .7671 | .2329 | .303 |
| 40 | K | .2295 | .2065 | 200.0 | .1846 | .7708 | .2292 | .298 |
| 41 | K | .2338 | .2085 | 199.1 | .1881 | .7730 | .2270 | .293 |
| | | | | Mean | .1869 | | | .295 |

## TABLE XII.

Showing the Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed (Equivalent) Salt-Concentration Ratio.

MIXED AQUEOUS PHASE 0.10 N. NaBr:KBr.

TEMPERATURE 25°C.

| No. | Amal. at start. | Analysis of the equilibrium amalgam |  |  | Milli-equiv. of metals per 10 g. Hg. | Mol fractions of amalgamated metals |  | $C_c$ |
|---|---|---|---|---|---|---|---|---|
|  |  | NaCl + KCl | $K_2PtCl_6$ | Hg. |  | Na | K |  |
| 1 | Na | .2025 | .2433 | 200.6 | .1590 | .6871 | .3129 | .455 |
| 2 | Na | .1933 | .2328 | 200.6 | .1517 | .6867 | .3133 | .456 |
| 3 | Na | .1891 | .2280 | 201.2 | .1480 | .6860 | .3140 | .458 |
| 4 | K | .1871 | .2253 | 200.5 | .1469 | .6863 | .3137 | .457 |
| 5 | K | .2104 | .2527 | 201.0 | .1656 | .6885 | .3115 | .453 |
| 6 | K | .2050 | .2473 | 201.6 | .1601 | .6858 | .3142 | .458 |
|  |  |  |  | Mean | .1552 |  |  | .456 |

MIXED AQUEOUS PHASE 0.20 N. NaBr:KBr.

| No. | Amal. at start. | NaCl + KCl | $K_2PtCl_6$ | Hg. | Milli-equiv. of metals per 10 g. Hg. | Na | K | $C_c$ |
|---|---|---|---|---|---|---|---|---|
| 7 | Na | .2244 | .2656 | 201.5 | .1756 | .6922 | .3078 | .445 |
| 8 | Na | .2193 | .2607 | 200.7 | .1722 | .6908 | .3092 | .448 |
| 9 | Na | .2128 | .2536 | 200.5 | .1672 | .6900 | .3100 | .449 |
| 10 | K | .2256 | .2703 | 201.4 | .1764 | .6883 | .3117 | .453 |
| 11 | K | .2255 | .2688 | 200.0 | .1776 | .6890 | .3110 | .451 |
| 12 | K | .2207 | .2629 | 200.0 | .1739 | .6904 | .3096 | .449 |
|  |  |  |  | Mean | .1738 |  |  | .449 |

MIXED AQUEOUS PHASE 0.50 N. NaBr:KBr.

| No. | Amal. at start. | NaCl + KCl | $K_2PtCl_6$ | Hg. | Milli-equiv. of metals per 10 g. Hg. | Na | K | $C_c$ |
|---|---|---|---|---|---|---|---|---|
| 13 | Na | .2258 | .2654 | 201.1 | .1771 | .6947 | .3053 | .439 |
| 14 | Na | .2275 | .2658 | 202.5 | .1734 | .6966 | .3033 | .435 |
| 15 | Na | .2236 | .2617 | 201.0 | .1755 | .6960 | .3040 | .436 |
| 16 | K | .2260 | .2650 | 201.2 | .1772 | .6951 | .3049 | .438 |
| 17 | K | .2245 | .2641 | 200.7 | .1765 | .6944 | .3056 | .440 |
| 18 | K | .2219 | .2597 | 200.0 | .1751 | .6960 | .3040 | .436 |
|  |  |  |  | Mean | .1758 |  |  | .437 |

## TABLE XII (continued)

Showing the Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed (Equivalent) Salt-Concentration Ratio.

MIXED AQUEOUS PHASE 1,00 N. NaBr:KBr.

TEMPERATURE 25°C.

| No. | Amal. at start | Analysis of the equilibrium amalgam |  |  | Milli-equiv. of metals per 10 g. Hg. | Mol fractions of amalgamated metals |  | $C_c$ |
|---|---|---|---|---|---|---|---|---|
|  |  | NaCl+ | $K_2PtCl_6$ | Hg. |  | Na | K |  |
| 19 | Na | .2228 | .2531 | 201.1 | .1753 | .7059 | .2941 | .416 |
| 20 | Na | .2259 | .2534 | 200.5 | .1784 | .7098 | .2902 | .409 |
| 21 | Na | .2197 | .2470 | 202.4 | .1719 | .7089 | .2911 | .411 |
| 22 | K | .2294 | .2593 | 201.1 | .1805 | .7075 | .2925 | .412 |
| 23 | K | .2255 | .2537 | 196.6 | .1816 | .7089 | .2911 | .411 |
| 24 | K | .2198 | .2473 | 199.2 | .1747 | .7089 | .2911 | .411 |
|  |  |  |  | Mean | .1771 |  |  | .412 |
|  |  | MIXED AQUEOUS PHASE 2.00 N. |  |  |  | NaBr:KBr. |  |  |
| 25 | Na | .2117 | .2224 | 198.3 | .1699 | .7294 | .2706 | .371 |
| 26 | Na | .2125 | .2207 | 201.3 | .1682 | .7330 | .2670 | .364 |
| 27 | Na | .2298 | .2401 | 199.8 | .1832 | .7310 | .2690 | .368 |
| 28 | K | .2255 | .2342 | 199.4 | .1752 | .7327 | .2673 | .365 |
| 29 | K | .2228 | .2331 | 202.0 | .1757 | .7309 | .2691 | .368 |
|  |  |  |  | Mean | .1746 |  |  | .367 |
|  |  | MIXED AQUEOUS PHASE 4.00 N. |  |  |  | NaBr:KBr. |  |  |
| 30 | Na | .2382 | .2167 | 201.0 | .1905 | .7681 | .2319 | .302 |
| 31 | Na | .2351 | .2134 | 198.7 | .1902 | .7687 | .2313 | .301 |
| 32 | Na | .2379 | .2150 | 200.5 | .1908 | .7697 | .2303 | .299 |
| 33 | K | .2396 | .2139 | 201.0 | .1918 | .7720 | .2280 | .295 |
| 34 | K | .2390 | .2146 | 200.8 | .1915 | .7711 | .2289 | .296 |
| 35 | K | .2325 | .2116 | 199.6 | .1872 | .7678 | .2322 | .302 |
|  |  |  |  | Mean | .1903 |  |  | .299 |

## TABLE XIII.

Showing the Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed (Equivalent) Salt-Concentration Ratio.

MIXED AQUEOUS PHASE 0.20 N. NaBr:KI.

TEMPERATURE 25°C.

| No. | Amal. at start | Analysis of the equilibrium amalgam | | | Milli-equiv. of metals 10 g. Hg. | Mol fractions of amalgamated metals | | $C_c$ |
|---|---|---|---|---|---|---|---|---|
| | | NaCl + KCl | $K_2PtCl_6$ | Hg. | | Na | K | |
| 1 | Na | .2137 | .2527 | 201.2 | .1675 | .6927 | .3073 | .444 |
| 2 | Na | .2168 | .2587 | 200.4 | .1705 | .6895 | .3105 | .450 |
| 3 | Na | .2175 | .2575 | 200.6 | .1705 | .6912 | .3088 | .447 |
| 4 | K | .2226 | .2658 | 201.5 | .1741 | .6895 | .3105 | .450 |
| 5 | K | .2223 | .2648 | 200.3 | .1749 | .6901 | .3099 | .449 |
| 6 | K | .2200 | .2613 | 201.1 | .1724 | .6912 | .3088 | .447 |
| | | | | Mean | .1716 | | | .448 |
| | | MIXED AQUEOUS PHASE 0.50 N. | | | | NaBr:KI. | | |
| 7 | Na | .2134 | .2498 | 201.5 | .1666 | .6962 | .3038 | .436 |
| 8 | Na | .2098 | .2440 | 202.4 | .1637 | .6980 | .3020 | .433 |
| 9 | Na | .2210 | .2573 | 200.9 | .1742 | .6979 | .3021 | .433 |
| 10 | K | .2190 | .2564 | 202.2 | .1709 | .6962 | .3038 | .436 |
| 11 | K | .2259 | .2615 | 202.2 | .1765 | .6997 | .3003 | .429 |
| 12 | K | .2201 | .2557 | 199.5 | .1742 | .6987 | .3013 | .431 |
| | | | | Mean | .1710 | | | .433 |
| | | MIXED AQUEOUS PHASE 1.00 N. | | | | NaBr:KI. | | |
| 13 | Na | .2074 | .2317 | 197.6 | .1658 | .7111 | .2889 | .406 |
| 14 | Na | .2135 | .2381 | 200.3 | .1689 | .7114 | .2886 | .405 |
| 15 | Na | .2306 | .2578 | 203.3 | .1797 | .7108 | .2892 | .407 |
| 16 | K | .2232 | .2487 | 201.3 | .1757 | .7118 | .2882 | .405 |
| 17 | K | .2227 | .2479 | 200.8 | .1758 | .7124 | .2876 | .403 |
| 18 | K | .2199 | .2472 | 201.6 | .1727 | .7092 | .2908 | .410 |
| | | | | Mean | .1731 | | | .406 |

## TABLE XIII. (continued)

Showing the Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed (Equivalent) Salt-Concentration Ratio.

MIXED AQUEOUS PHASE 2.00 N. NaBr:KI.

TEMPERATURE 25°C.

| No. | Amal. at start | Analysis of the equilibrium amalgam | | | Milli-equiv. of metals 10 g. Hg. | Mol fractions of amalgamated metals | | $C_c$ |
|---|---|---|---|---|---|---|---|---|
| | | NaCl+ KCl | $K_2PtCl_6$ | Hg. | | Na | K | |
| 19 | Na | .2424 | .2496 | 200.8 | .1924 | .7352 | .2648 | .360 |
| 20 | Na | .2475 | .2531 | 202.1 | .1954 | .7374 | .2626 | .356 |
| 21 | Na | .2394 | .2468 | 200.5 | .1903 | .7350 | .2650 | .360 |
| 22 | K | .2332 | .2403 | 199.8 | .1860 | .7352 | .2648 | .360 |
| 23 | K | .2339 | .2405 | 202.5 | .1841 | .7357 | .2643 | .359 |
| 24 | K | .2289 | .2372 | 201.7 | .1808 | .7334 | .2666 | .364 |
| | | | | Mean | .1882 | | | .360 |
| MIXED AQUEOUS PHASE 4.00 N. | | | | | | NaBr:KI. | | |
| 25 | Na | .2319 | .1953 | 200.3 | .1870 | .7862 | .2138 | .272 |
| 26 | Na | .2378 | .2027 | 201.4 | .1906 | .7837 | .2163 | .276 |
| 27 | Na | .2414 | .2071 | 199.8 | .1955 | .7818 | .2182 | .278 |
| 28 | K | .2855 | .2371 | 211.3 | .2184 | .7893 | .2107 | .267 |
| 29 | K | .2798 | .2372 | 209.4 | .2158 | .7848 | .2152 | .274 |
| 30 | K | .2882 | .2539 | 209.4 | .2217 | .7758 | .2242 | .288 |
| | | | | Mean | .2048 | | | .276 |

## TABLE XIV.

Showing the Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed (Equivalent) Salt-Concentration Ratio.

MIXED AQUEOUS PHASE 0.20 N. NaI:KI.

TEMPERATURE 25°C.

| No. | Amal. at start | Analysis of the equilibrium amalgam | | | Milli-equiv. of metals per 10 g. Hg. | Mol fractions of amalgamated metals | | $C_c$ |
|---|---|---|---|---|---|---|---|---|
| | | NaCl+ KCl | $K_2PtCl_6$ | Hg. | | Na | K | |
| 1 | Na | .2023 | .2422 | 202.0 | .1577 | .6886 | .3114 | .452 |
| 2 | Na | .2125 | .2526 | 203.4 | .1647 | .6909 | .3091 | .447 |
| 3 | Na | .2099 | .2500 | 202.4 | .1631 | .6902 | .3098 | .449 |
| 4 | K | .2038 | .2411 | 199.0 | .1620 | .6924 | .3076 | .444 |
| 5 | K | .1845 | .2198 | 200.5 | .1457 | .6902 | .3098 | .449 |
| 6 | K | .2220 | .2652 | 202.9 | .1724 | .6894 | .3106 | .450 |
| | | | | Mean | .1609 | | | .448 |
| MIXED AQUEOUS PHASE 0.50 N. | | | | | | NaI: KI. | | |
| 7 | Na | .2209 | .2542 | 200.4 | .1742 | .7015 | .2985 | .425 |
| 8 | Na | .2100 | .2436 | 200.6 | .1654 | .7005 | .2995 | .427 |
| 9 | Na | .1523 | .1784 | 190.4 | .1262 | .6965 | .3035 | .437 |
| 10 | K | .2197 | .2540 | 201.0 | .1732 | .7002 | .2998 | .428 |
| 11 | K | .2285 | .2668 | 202.7 | .1779 | .6970 | .3030 | .434 |
| 12 | K | .2194 | .2543 | 201.7 | .1719 | .6995 | .3005 | .431 |
| | | | | Mean | .1648 | | | .430 |
| MIXED AQUEOUS PHASE 1.00 N. | | | | | | NaI:KI. | | |
| 13 | Na | .2176 | .2392 | 196.2 | .1759 | .7160 | .2840 | .397 |
| 14 | Na | .2211 | .2430 | 200.6 | .1748 | .7159 | .2841 | .397 |
| 15 | Na | .2171 | .2400 | 200.2 | .1715 | .7144 | .2856 | .400 |
| 16 | K | .2197 | .2421 | 198.0 | .1759 | .7152 | .2848 | .398 |
| 17 | K | .2247 | .2478 | 200.5 | .1777 | .7151 | .2849 | .398 |
| 18 | K | .2184 | .2416 | 199.4 | .1736 | .7136 | .2864 | .401 |
| | | | | Mean | .1749 | | | .398 |

## TABLE XIV. (continued)

Showing the Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed (Equivalent) Salt-Concentration Ratio.

MIXED AQUEOUS PHASE 2.00 N. NaI:KI.

TEMPERATURE 25°C.

| No. | Amal. at start. | Analysis of the equilibrium amalgam |  |  | Milli-equiv. of metals per 10 g. Hg. | Mol fractions of amalgamated metals |  | $C_c$ |
|---|---|---|---|---|---|---|---|---|
|  |  | NaCl + KCl | $K_2PtCl_6$ | Hg. |  | Na | K |  |
| 19 | Na | .2238 | .2263 | 200.3 | .1783 | .7402 | .2598 | .350 |
| 20 | Na | .2268 | .2282 | 200.2 | .1809 | .7419 | .2581 | .348 |
| 21 | Na | .2239 | .2263 | 200.5 | .1782 | .7403 | .2597 | .350 |
| 22 | K | .2262 | .2284 | 199.3 | .1812 | .7408 | .2592 | .350 |
| 23 | K | .2310 | .2243 | 201.0 | .1834 | .7396 | .2604 | .352 |
| 24 | K | .2270 | .2292 | 200.7 | .1805 | .7409 | .2591 | .350 |
|  |  |  |  | Mean | .1804 |  |  | .350 |

MIXED AQUEOUS PHASE 4.00 N. NaI:KI.

| No. | Amal. at start. | NaCl + KCl | $K_2PtCl_6$ | Hg. | Milli-equiv. of metals per 10 g. Hg. | Na | K | $C_c$ |
|---|---|---|---|---|---|---|---|---|
| 25 | Na | .2259 | .1818 | 200.5 | .1825 | .7934 | .2066 | .260 |
| 26 | Na | .2301 | .1956 | 201.0 | .1853 | .7820 | .2180 | .280 |
| 27 | Na | .2244 | .1880 | 199.0 | .1804 | .7877 | .2123 | .269 |
| 28 | K | .2274 | .1800 | 201.5 | .1849 | .7999 | .2001 | .250 |
| 29 | K | .2251 | .1798 | 201.5 | .1810 | .7981 | .2019 | .253 |
| 30 | K | .2293 | .1866 | 201.9 | .1838 | .7940 | .2060 | .259 |
|  |  |  |  | Mean | .1830 |  |  | .262 |

this, the small individual differences in concentration do not warrant a correction of the $C_c$ values. In every equilibrium studied the value of the expression, $C_c$, decreases with increasing concentration of the mixed (equivalent) salt solution. The results are best studied by reference to the curves in Figure 3 where the values of $C_c$ are plotted against those of the total normal salt concentration. It will be observed that the $C_c$ values change the more rapidly the higher the atomic weight of the halogen.

5. *The Ion-Fraction Changes Which Take Place Upon Increasing the Concentration of Equivalent Aqueous Mixtures of Sodium and Potassium Chlorides, Bromides and Iodides*.- It has been shown in the theoretical section that, given the value of k (Equation 6), the ion fractions of the metals in the individual aqueous mixtures may be calculated by means of the expressions

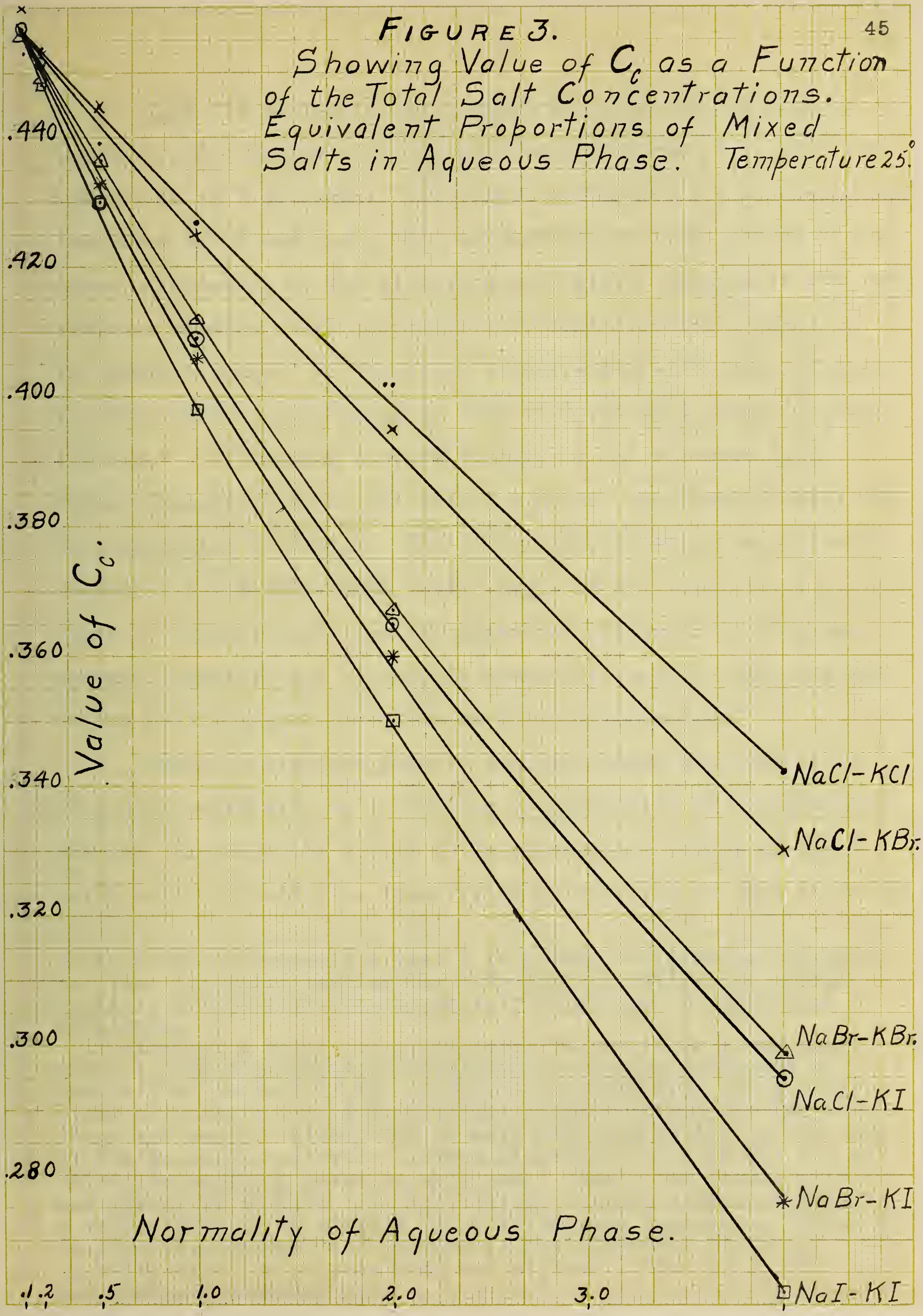
$$(K+) = \frac{(K_{Hg})}{(K_{Hg}) + k(Na_{Hg})}, \text{ and} \qquad (9)$$

$$(Na+) = 1 - (K+).$$

But, since we do not know either the respective degrees of dissociation of the sodium and potassium hydrargyrides in the mercurial phase or the simple (unhydrated) ion fractions of these metals in the aqueous phase, there does not seem to be any good prospect for the determination of the value of k. We are therefore compelled to start with some assumption concerning the value of k, in order, with that as a basis, to study the ion-fraction changes which accompany changes in salt-concentration in the aqueous phase.

FIGURE 3.

Showing Value of $C_c$ as a Function of the Total Salt Concentrations. Equivalent Proportions of Mixed Salts in Aqueous Phase. Temperature 25°.



With the assumption as a starting point that in each of the equivalent sodium and potassium salt mixtures at a total concentration of 0.20 normal, the simple sodium-ion and potassium-ion fractions are 0.500 and 0.500, we can then at least determine, by means of Equation 9, the direction and relative degree of the ion-fraction changes which accompany salt-concentration changes in the aqueous phase. On the basis of the assumption just referred to, the value of k is equal to that of $C_c$ at 0.20 normal concentration.* If instead of 0.20 normal, we had selected 0.10 normal concentration as the starting point, the results would not be essentially different. The former concentration was selected because (1) the individual values $Na_{Hg}$ and $K_{Hg}$ (calculated on the basis of the mol fractions of sodium and potassium in 10 grams of mercury) checked very closely in this case, and (2) runs for all of the salt mixtures were made at this concentration.

From the previous data it has been shown that the value of Cc decreases with an increasing concentration of the amalgam, and upon plotting the values of $C_c$ against the values of the total salt concentration (see Figure 2) for each of five different

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* It should be emphasized that k is a real equilibrium constant, and that its value remains the same for all ratios and concentrations of the different mixed salt solutions of sodium and potassium.

In assuming a value for k, in order to use it as a stepping stone in the ion-fraction calculations, we have preferred to assume that in each of the different salt mixtures, at an equivalent salt ratio and at 0.20 normal concentration, the ion fractions are equal; rather than to make this assumption in the case of the chloride--chloride mixture alone, and to base all the calculations on the k value so obtained. While the former method may appear to involve a contradiction, in that several different k values seem to be assumed, it nevertheless enables us better to compare the ion-fraction changes in the different mixtures, since in every case the calculations are started on the same basis at 0.20 normal concentration.

specific amalgam concentrations, a series of five parallel curves is obtained; and the statement may be made that the change in the value of $C_c$ caused by varying the concentration of the amalgam is independent of the change caused by increasing the total salt concentration at a fixed (equivalent) concentration ratio. If this is true, the ion-fraction values found for mixed (equivalent) solutions of sodium and potassium chloride at specific normal concentrations should be the same regardless of the concentration of the equilibrium amalgam. This is shown to be true in Table XV, in which are given the $K^+$-ion fractions calculated at different amalgam concentrations for various equivalent mixtures of sodium and potassium chlorides.

TABLE XV.

Showing the Ion-Fraction Changes Which Accompany Salt-Concentration Changes in Equivalent Aqueous Mixtures of Sodium and Potassium Chlorides at 25°C.

| Normality of mixed aqueous solution. | $C_c$ value at x milli-equiv. of metals per 10 g. Hg. | | | $K^+$ fraction calculated on the assumption that in 0.20 N equivalent mixture, n (Equation 7)=1 | | |
|---|---|---|---|---|---|---|
| | x=0.1 | x=0.3 | x=0.5 | x= 0.1 | x= 0.3 | x=0.5 |
| 0.20 | .458 | .435 | .411 | .500 | .500 | .500 |
| 0.50 | .449 | .426 | .403 | .495 | .495 | .495 |
| 1.00 | .435 | .412 | .390 | .487 | .486 | .487 |
| 2.00 | .407 | .384 | .360 | .470 | .469 | .466 |
| 4.00 | .354 | .331 | .307 | .436 | .432 | .429 |

Table XVI shows the ion-fraction changes which accompany salt-concentration changes in equivalent aqueous mixtures of sodium and potassium chlorides, bromides and iodides at 25°C., and in Figure 4 these values are plotted against the total salt concentration. From these curves it is evident that the

potassium-ion fraction decreases, while the sodium-ion fraction correspondingly increases, with increasing total salt concentration. These changes take place the more rapidly the higher the atomic weight of the halogen.

## TABLE XVI.

Showing the Ion-Fraction Changes Which Accompany Salt-Concentration Changes in Equivalent Aqueous Mixtures of Sodium and Potassium Chlorides, Bromides and Iodides at 25°C.

NaCl:KCl.

| Normality of mixed aqueous solutions | $C_c$ | Ion fractions, calculated on the assumption that in 0.20 N equivalent mixture, n (Equation 7)=1 | |
|---|---|---|---|
| | | ($Na^+$) | ($K^+$) |
| 0.10 | 0.453 | 0.501 | 0.499 |
| 0.20 | 0.454 | 0.500 | 0.500 |
| 0.50 | 0.439 | 0.507 | 0.493 |
| 1.00 | 0.427 | 0.515 | 0.485 |
| 2.00 | 0.402 | 0.530 | 0.470 |
| 4.00 | 0.342 | 0.570 | 0.430 |
| NaCl:KBr. | | | |
| 0.10 | 0.461 | 0.496 | 0.504 |
| 0.20 | 0.453 | 0.500 | 0.500 |
| 0.50 | 0.445 | 0.505 | 0.495 |
| 1.00 | 0.425 | 0.516 | 0.484 |
| 2.00 | 0.395 | 0.534 | 0.466 |
| 4.00 | 0.330 | 0.579 | 0.421 |
| NaCl:KI. | | | |
| 0.10 | 0.457 | 0.497 | 0.503 |
| 0.20 | 0.452 | 0.500 | 0.500 |
| 0.50 | 0.430 | 0.513 | 0.487 |
| 1.00 | 0.409 | 0.525 | 0.475 |
| 2.00 | 0.365 | 0.553 | 0.447 |
| 4.00 | 0.295 | 0.605 | 0.395 |

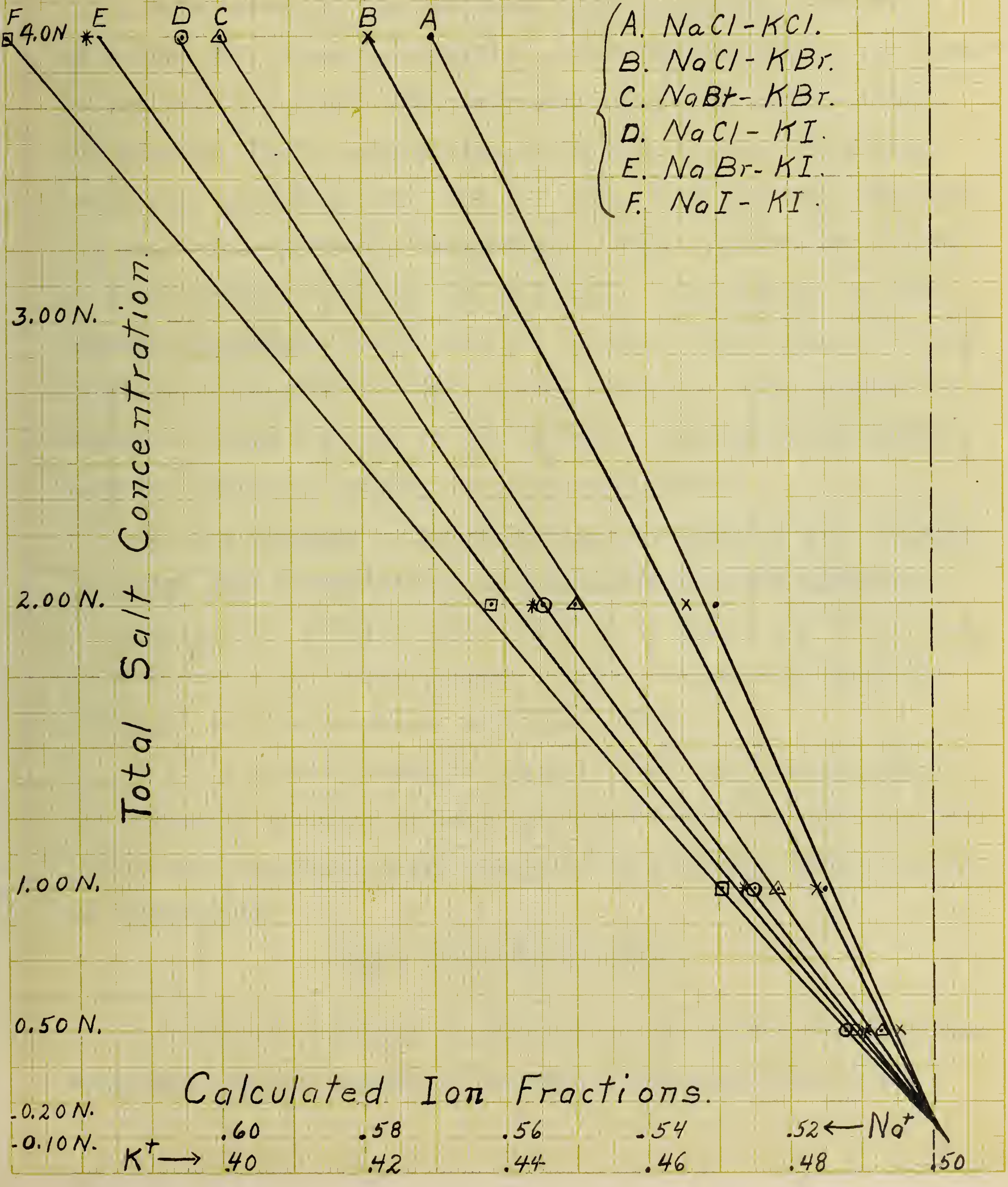
## TABLE XVI (continued)

Showing the Ion-Fraction Changes Which Accompany Salt-Concentration Changes in Equivalent Aqueous Mixtures of Sodium and Potassium Chlorides, Bromides and Iodides at 25°C.

NaBr:KBr.

| Normality of mixed aqueous solutions | $C_c$ | Ion fractions, calculated on the assumption that in 0.20 N equivalent mixture, n(Equation 7)=1 | |
|---|---|---|---|
| | | ($Na^+$) | ($K^+$) |
| 0.10 | 0.456 | 0.496 | 0.504 |
| 0.20 | 0.449 | 0.500 | 0.500 |
| 0.50 | 0.437 | 0.507 | 0.493 |
| 1.00 | 0.412 | 0.521 | 0.479 |
| 2.00 | 0.367 | 0.550 | 0.450 |
| 4.00 | 0.299 | 0.600 | 0.400 |
| | | NaBr:KI | |
| 0.20 | 0.448 | 0.500 | 0.500 |
| 0.50 | 0.433 | 0.509 | 0.491 |
| 1.00 | 0.406 | 0.526 | 0.474 |
| 2.00 | 0.360 | 0.555 | 0.445 |
| 4.00 | 0.276 | 0.619 | 0.381 |
| | | NaI:KI | |
| 0.20 | 0.448 | 0.500 | 0.500 |
| 0.50 | 0.430 | 0.510 | 0.490 |
| 1.00 | 0.398 | 0.530 | 0.470 |
| 2.00 | 0.350 | 0.561 | 0.439 |
| 4.00 | 0.262 | 0.630 | 0.370 |

FIGURE 4.
Showing Ion Fractions of Sodium and Potassium as a Function of Total Salt Concentration in Mixed Equivalent Aqueous Solutions of Their Chlorides, Bromides and Iodides. Temperature 25°C.



# V. DISCUSSION

This investigation has shown that in equivalent mixtures of sodium and potassium chlorides, bromides and iodides the simple potassium-ion fraction ($K^+$) decreases, while the simple sodium-ion fraction ($Na^+$) correspondingly increases, with increasing total salt concentration. In the case of the chloride mixtures, the only ones previously investigated, these results agree with those previously obtained (18) and (25). The results of this present investigation have brought forth the additional fact that these same ion-fraction changes take place the more rapidly the higher the atomic weight of the halogen. The following explanation is offered to account for these phenomena.

1. <u>The Decrease of the Potassium-ion Fraction with Increasing Total Salt Concentration in Equivalent Chloride Mixtures.</u>- The ion-fraction changes above referred to may be due to any one, or both of the following causes: (a) the existence of hydrated ions, and (b) the existence of complex ions.

(a) It is well known for example that the ions of sodium and potassium are more or less hydrated in solution (26) and very likely also the non-ionized molecules that furnish these ions may be hydrated as

$$MeX + nH_2O \rightleftharpoons [Me(H_2O)n]X.$$

It has already been pointed out in the introductory section that such hydrated compounds may also yield intermediate and

complex ions, in varying quantities or degrees of stability. There is good evidence that many complexes, not sufficiently insoluble or stable to be isolated, exist in solution. Kendall (27) has quite recently emphasized the ideas of Werner in regard to the mechanism of the ionization process. "Ionization is preceded by combination between solvent and solute and is, indeed, a consequence of such combination, and the two phenomena proceed in parallel". Such ideas are in particular harmony with Werner's theory of bases (28) and acids, and with his theory of the formation of higher-order compounds (29). Hydration is evidently a case of complex formation.

(b) Complexes may be formed in other ways than through the agency of water. The alkali halides are capable of forming addition compounds with one another, as well as with other substances, and these may ionize to give complex ions (30). Furthermore, the alkali halides show a tendency to polymerize (31). In recent years evidence (bases upon absorption spectra data) has been brought forth which tends to show that the alkali metals, thru the agency of secondary valence unions, are capable of effecting closed ring structures, with the formation of inner complex salts (32). Through conductance studies the alkali salts of certain organic acids Lifschitz (33) has arrived at a similar conclusion.

Evidently then, the fact that we may have hydrated ions and molecules, addition and polymerized compounds, and many complexes capable of furnishing ions of various species, makes any speculations as to just which complexes exist in solution more or less futile. If, however, the potassium tends to form complex ions

more readily than the sodium, in equivalent aqueous mixtures of their chlorides, we should expect the concentration of the simple potassium ion to be more rapidly diminished by mass action than that of the simple sodium ion, upon increasing the total salt concentration.

2. The Further Decrease of the Potassium-ion Fraction with Increasing Atomic Weight of the Halogen in the Mixed Salt Solutions.- In the case of chlorine, bromine and iodine, it is well known that the tendency towards complex formation increases with the atomic weight of the halogen. Thus we find iodine forming a great many compounds in which it functions as the central nucleus (29),(34),(35) and (36).

In short, owing to the greater tendency of potassium than of sodium, and of iodine and bromine than of chlorine to form complexes, we should expect the simple potassium-ion fraction to decrease with increasing total salt concentration; and also, that this decrease should take place the more rapidly, the higher the atomic weight of the halogen.

## VI. SUMMARY

1. At a fixed total salt concentration, the value of the equilibrium expression, $C_c$, decreases with the increase in the concentration of the amalgam.

2. At fixed amalgam and total salt concentrations, but with varying salt ratio, the value of the equilibrium expression, $C_c$, is constant.

3. At a fixed amalgam concentration, the value of the equilibrium expression, $C_c$, <u>decreases</u> with <u>increasing</u> concentration of the mixed (equivalent) salt solutions.

4. Ion-fraction calculations are offered for solutions containing the salts in equivalent proportions. It is found that the simple potassium-ion fraction decreases, while the sodium-ion fraction correspondingly increases, with increasing total salt concentration. These changes take place the more rapidly the higher the atomic weight of the halogen.

5. The results of the investigation, in so far as the salt mixtures are concerned, have been shown to be in harmony with A. Werner's conceptions concerning the formation and dissociation of higher order compounds.

## BIBLIOGRAPHY.

(1) G.McP.Smith and T.R.Ball, J. Am. Chem. Soc., 39, 179 (1917).

G.McP.Smith and S.A.Braley, J. Am. Chem. Soc., 39, 1545 (1917).

G.McP.Smith and E.A.Rees, J. Am. Chem. Soc., 40,1802 (1918).

(2) G.McP.Smith, J. Am. Chem. Soc., 32, 502 (1910).

G.McP.Smith, J. Am. Chem. Soc., 35, 39 (1913).

(3) G.McP.Smith, J. Am. Chem. Soc., 29, 844 (1907).

(4) G.McP.Smith, Z. anorg. Chem., 58, 381 (1908).

A summary of the literature concerning the crystalline compounds may be found in this paper.

(5) W.Ramsay, J. Chem. Soc., 55, 521 (1889)

(6) G.McP.Smith, J. Am. Chem. Soc., 29, 844 (1907).

Am. Chem. J., 36, 124 (1906).

" " " 37, 508 (1907).

Z.anorg. Chem.,58,381 (1908).

" " " 88,161 (1914).

J. Am. Chem. Soc. 36, 859 (1914).

" " " " 37, 76 (1915).

E. Bechmann and O. Liesch, Z. anorg. Chem., 89, 171 (1914).

(7) Cf. G.McP.Smith, J. Am. Chem. Soc. 37, 80, footnote 1 (1915).

(8) Svannte Arrhenius, Z. physik. Chem., 2, 284 (1888).

(9) F. Barnwater, Z. physik. Chem., 28, 427 (1899).

(10) MacGregor, Archibald, McIntosh and McKay, Trans. Nova Scotia Inst. Sci., 9 and 10 (1895-1899).

(11) M.S. Sherrill, J. Am. Chem. Soc., 32, 741 (1910).

(12) C. Sandonnini, Atti. Inst. Veneto, 74, 519 (1915);

Gazz. chim. ital., (2) 46, 205 (1916).

(13) G.M.J.McKay, J. Am. Chem. Soc., 33, 308 (1911).

(14) N.E.Loomis and M.R.Meacham, J. Am. Chem. Soc., 38, 2310(1916).

(15) N.E.Loomis, J.L.Essex and M.R.Meacham, J. Am. Chem. Soc., 39, 1133 (1917).

(16) G.McP.Smith and S.A.Braley, J. Am. Chem. Soc., 39, 1545 (1917); 40, 197 (1918).

(17) G.McP.Smith and E.A.Rees, J. Am. Chem. Soc., 41, 1802 (1918).

(18) G.McP.Smith and T.R.Ball, J. Am. Chem. Soc., 39, 179 (1917).

(19) G.McP.Smith, J. Am. Chem. Soc., 32, 502 (1910).

(20) G.N.Lewis, Proc. Amer. Acad., 37, 49 (1901);
Proc. Amer. Acad., 43, 259 (1907);
Z. physik. Chem., 38, 205 (1901);
Ibid., 61, 129 (1907).

(21) G.A.Hulett and R.E.DeLury, J. Am. Chem. Soc., 30, 1812(1910).
J.L.Crenshaw, J. Phys. Chem., 14, 158 (1910).
J.H.Hildebrand, Trans. Am. Elec. Soc., 22, 319 (1912).
J. Am. Chem. Soc., 35, 501 (1913).
See also reference (6).

(22) G.N.Lewis, J. Am. Chem. Soc., 30, 668 (1903).
S.J.Bates, J. Am. Chem. Soc., 37, 1428 (1915).
D.A.MacInnes and K. Parker, J. Am. Chem. Soc., 37, 1456 (1915).

(23) Cf. R.C.Tolman and A.L.Ferguson, J. Am. Chem. Soc., 34, 232 (1912).

(24) G.McP.Smith and H.C.Bennett, J. Am. Chem. Soc., 31, 802 (1909).

(25) G.McP.Smith, J. Am. Chem. Soc., 35, 39 (1913).

(26) Arrhenius, "Theories of Solutions", pp. 184-195.
E.W.Washburn, Tech. Quart., 21, 360 (1908).
Cf. G.McP.Smith, J.Am.Chem.Soc., 37, 722 (1915).

(27) J.Kendall and J.E.Booge, J. Am. Chem.Soc., 39, 2323 (1917).

(28) A.Werner, Ber., 40, 4133-45 (1907).

(29) A.Werner,"Neuere Auschauungen a.d. Gebiete d.anorg.Chemie," Braunschweig (1913).

(30) Cf.Werner,"Neuere Auschauungen, etc.,p.28. Joannis, Compt. rend. 112, 338 (1891). Abezz and Riesenfeld,Z.physik. Chem., 40, 84 (1902).

(31) See, Zannovich-Tessarin, Z. physik, Chem., 19, 251 (1896).
Andrews and Ende, Ibid., 17, 136 (1895).
E.W.Washburn, Trans. Am. Electrochem. Soc.,21, 137 (1912).

(32) Hantzsch, Ber., 43, 3049 (1910).
Hantzsch and Voigt, Ber., 45, 85 (1912).

(33) Lifschitz, Z. physik. Chem., 87, 567 (1914).

(34) See L. Gattermann, "The Practical Methods of Organic Chemistry" MacMillan Co. (1914) p.244, Also, C. Willgerodt, "Die Organischen Verbindungen mit Mehrwertigen Jod". F.Enke (1914).

(35) Cf. A. Hantzsch, Ann. 349, 1 (1906). For bromine compounds, see D. McIntosh, J. Chem. Soc., 87 784 (1905).

(36) See K. Hellwig, Z. anorg. Chem., 25, 157 (1900) for examples of complex compounds with netative central atoms as $(JAg_3)^+$, etc.

## VII. BIOGRAPHY.

The writer of this thesis received his early education in the public schools of Helena, Montana. He received the degree of Bachelor of Arts in Chemistry at the University of Montana in 1915. The senior thesis consisted of a study of the "Copper in the Flora of a Copper-Tailing Region", (J.Am. Chem. Soc., 39, 811 (1917), and was carried out under the direction of Professor W.G.Bateman. During the academic year of 1912-1913 he was a student at the University of Utah. He was Student Assistant in Chemistry at the University of Montana during the years 1913-1915.

In 1915 he entered the Graduate School of the University of Illinois as a Graduate Assistant in Chemistry, and received in June 1917 the degree of Master of Arts. The thesis was on "An Analytical Study of Flue and Bag-House Dusts from a Certain Smelting Plant", and was carried out under the direction of Professor G.McP.Smith. During the academic years 1916-1918 he held the position of Assistant in Chemistry in the University of Illinois, and during 1918-1919 that of Fellow in Chemistry at the same place.

During his four years of graduate work the writer has been engaged in the study of Analytical - Inorganic and Physical Chemistry, and of Physics.